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PROCEEDINGS OF

THE ROYAL SOCIETY.

Section A.—Mathematical and Physical Sciences.

The Combination of Hydrogen and Oxygen on the Surface of Silica and its Relation to the Propagation of Reaction Chains in the Gas.

By W. L. Garstang and C. N. Hinshelwood, F.R.S.

(Received July 6, 1931.)

Introduction.

The combination of hydrogen and oxygen, at temperatures between 400° and 600° C. in vessels of porcelain or silica involves several different processes.* At the lower temperatures a surface reaction tends to predominate, which on a silica surface is approximately of the first order. At higher temperatures and higher pressures a chain reaction occurs in the gas phase. At temperatures greater than 450° C. there also exists a lower and an upper limit of pressure below and above which reaction is slow and between which explosion occurs. The transition from slow reaction to explosion is an abrupt one, the limits representing discontinuities of some kind.

The upper limit is almost the same in reaction vessels of silica or porcelain and is nearly independent of their dimensions.

The occurrence of the explosion, however, is not independent of the vessel wall, since when crossed streams of hydrogen and oxygen at suitable partial pressures and temperatures are mixed in an atmosphere of nitrogen, without being allowed to touch a solid surface, the characteristic "low pressure" ignition does not take place. The upper limit is lowered by an increase in the ratio of hydrogen to oxygen and by the presence of argon, steam and other substances. There is also evidence that it is displaced by "pre-treatment" of the vessel walls with hydrogen or iodine, but this effect is rather slight and somewhat uncertain.

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* For review of previous literature see Garstang and Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 130, p. 640 (1931).

With regard to the interpretation of this phenomenon, it seems to be clear that the explosion is determined by "branching" reaction chains. The initiation of these apparently demands the presence of a suitable surface; but the point at which they are no longer able to branch effectively seems equally definitely to be determined by deactivation of active molecules in the gas phase. Recently Alyea* has attempted to explain the upper limit by assuming an abrupt change in the layer of gas adsorbed on the vessel wall. He supposes that the chains are initiated by hydrogen atoms, formed in a reaction of hydrogen at or with the vessel wall. He assumes that above the upper limit a complete layer of hydrogen covers the wall, and that very few hydrogen atoms escape, so that the resulting gas reaction is extremely slow. As the pressure is reduced the hydrogen is slightly desorbed, and at the upper limit oxygen can penetrate and make a "flank attack," so that the remaining hydrogen is swept from the wall. The rate of escape of hydrogen atoms is now great enough to cause explosion.

This hypothesis is an interesting one, since it not only explains the existence of an abrupt limit nearly independent of the dimensions of the vessel, but it also explains possible "pre-treatment" effects connected with the vessel wall. There are, however, as shown later in this paper, grave and possibly conclusive objections to it.

In the earlier stages of our investigations the kinetics of the surface reaction itself appeared to offer much less interest than the phenomena of explosion and of the high-pressure chain reaction in the gas.

In view, however, of the fact that something necessary for the explosion—

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* 'J. Amer. Chem. Soc.,' vol. 53, p. 1324 (1931).

We must here correct a statement made by Alyea about some of the results published from this laboratory. On p. 1327 he makes a comparison of two sets of data which he says were obtained "under comparable extent and particle size of packing material." In point of fact the packing referred to under "early publications" consisted in a complete filling of the reaction vessel with powdered porcelain ('Proc. Roy. Soc.,' A, vol. 119, p. 592 (1928)), while in the "later publications" the packing consisted of some cylindrical tubes (*Ibid.*, vol. 122, p. 616). The tubular packing damps down the high-pressure chain reaction in the gas very effectively indeed (since this depends on the square of the tube diameter) without causing a corresponding increase of surface. The cruder method used in the earlier experiments of adding powdered material, stops the chain reaction in the gas, but gives such a large increase of surface that the heterogeneous reaction becomes very fast. Thus no sort of comparison can be made between the two cases.

whether hydrogen atoms or not—is first formed on the surface, and in view of Alyea's hypothesis about the upper limit, it now seemed desirable to study the surface reaction in more detail, since this would yield information concerning the adsorbed gas layers which take part in the reaction.

. *Combination of Hydrogen and Oxygen at the Surface of Silica.*

The reaction vessel used was a silica bulb packed with small spheres of silica. At a temperature of 550° C. at which all the experiments were made, the amount of gas reaction occurring is quite negligible in comparison with the surface reaction.* Measurements were made to determine how the initial rate of reaction varied when the initial pressure of one gas was varied, that of the other being constant. Four series of experiments were carried out. In Series I to III, the hydrogen was admitted first; the silica immediately takes up an appreciable quantity of hydrogen, but experiments showed that after the hydrogen has been in the bulb for a few seconds the rate of absorption is very slow indeed, and can have no appreciable effect on the measurements. Therefore in these series the initial rate of reaction is calculated as the mean rate for the first few millimetres pressure change expressed as millimetres pressure change per hour. In Series IV the oxygen was admitted first. Under these conditions the rate of reaction showed an apparent small increase for the first 2 or 3 mm. pressure change. Therefore in this series the initial rate of reaction is calculated as the mean rate between 3 mm. and 6 mm. pressure change.

The results of the four series are given below in the table. Owing to possible "drifts," due to temporary or perhaps permanent changes in the silica surface, the individual results of one series are not strictly comparable with those of another, although the general result of one series may be compared with that of another.

It is seen that the rate of reaction is almost independent of the oxygen concentration, except at low pressures. This shows that the adsorbed oxygen layer which takes part in the reaction is almost completely saturated except at small concentrations. On the other hand, the rate varies approximately in direct proportion to the hydrogen concentration. This shows that hydrogen is only sparingly adsorbed on the centres which catalyse the surface reaction. The significance of these and other results will now be discussed.

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* In this bulb the upper explosion limit was found to be 93 mm. for $2H_2 + O_2$, very close to that found by Thompson and Hinshelwood for an unpacked bulb, 99 mm.

Table.—The Combination of Hydrogen and Oxygen on a Silica Surface.
(Sphere-packed silica bulb at 550° C.)

Series I.		Series III.	
$H_2 = 400$ mm., O_2 varied.		$H_2 = 120$ mm., O_2 varied.	
Oxygen pressure.	Initial rate of reaction.	Oxygen pressure.	Initial rate of reaction.
mm.	mm. per hour.	mm.	mm. per hour.
260	42·3	198	16·2
200	46·4	151	15·8
	44·0	148	17·0
149	48·0	109	17·2
101	48·7	99	16·7
62	34·3	81	15·5
20	37·5	60	13·2
		40	12·6
		21	11·0

Series II.		Series IV.	
$O_2 = 200$ mm., H_2 varied.		$O_2 = 120$ mm., H_2 varied.	
Hydrogen pressure.	Initial rate of reaction.	Hydrogen pressure.	Initial rate of reaction.
mm.	mm. per hour.	mm.	mm. per hour.
400	70·6	399	34·8
300	41·8	241	21·0
200	39·1	91	10·0
100	13·0	38	6·8

Discussion of the Results.

The above results suggest that there cannot be any direct correlation between the surface reaction and the propagation of chains in the low-pressure region, since there are no abrupt changes in the curves of the kind which would be expected if there were any such correlation. If, for example, Alyea's explanation of the upper limit is correct, then the hydrogen sheath which he considers is certainly not the one adsorbed on the centres which catalyse the surface reaction; for the results definitely show that in this reaction there is no saturated hydrogen layer in which an abrupt change of the kind he assumes could take place.

There is, however, a saturated oxygen layer adsorbed on the centres in question, and Alyea's hypothesis might be modified by interchanging the rôles of hydrogen and oxygen. There are, however, other considerations which make it extremely difficult to accept the hypothesis ; these are as follows.

A number of experiments were made with the sphere-packed silica bulb at 550° C., where the upper explosion pressure was 93 mm. for equivalent amounts of the gases. In each experiment 120 mm. of either hydrogen or oxygen was first admitted into the previously-evacuated bulb, and to this was slowly added the other gas. No explosion ever occurred during the admission of the second gas. According to Alyea's hypothesis, when hydrogen is added to oxygen the conditions are favourable for the rapid generation of hydrogen atoms which will lead to explosion, the hydrogen pressure being much less than that at which the hydrogen sheath breaks down. Explosion does not however occur. If we invert the hypothesis and suppose that an oxygen sheath prevents the generation or escape into the gas phase of atoms, molecules or active radicles, then explosion should occur when the addition is reversed. It is difficult to believe that both an oxygen sheath and a hydrogen sheath, each having the properties described, can exist under similar conditions and but very slightly different circumstances.

The interpretation of the above facts by means of the hypothesis of deactivation in the gas phase, presents no difficulties. In terms of this it is quite understandable that excess of either gas, or of a foreign gas, should prevent the explosion, however low the partial pressure of the other. Therefore it seems reasonable to adopt the hypothesis of deactivation in the gas at the upper limit at least until further evidence is forthcoming.

This hypothesis has to be reconciled with possible "pre-treatment" effects. These are connected with the starting rather than the stopping of the chains. The chains start on the surface ; they are broken in the gas. Over a wide range the upper pressure limit can be independent of the number of chains actually starting since it is the condition for *branching* rather than the original number which determines the explosion. The limit is in fact nearly the same in a vessel of porcelain as in one of silica. But this does not hold over an indefinite range. If no chains started there would naturally be no explosion. When very few start, the upper limit is low. But with increasing numbers the condition for branching determines the limit more and more completely, *i.e.*, gas phase deactivation plays the principal part. But there may well be an intermediate condition where the number starting, and thus the state of the surface, can slightly displace the upper limit.

The Behaviour of Mixtures of Hydrogen and Oxygen in a Reaction Vessel of Aluminium.

The apparatus used in the present investigation was similar to that described in previous communications, except that an aluminium reaction vessel was used; the reactions were followed manometrically.

This vessel, having an internal volume of about 300 c.c., was constructed with great difficulty. It was not absolutely gas-tight, but the leaks were sufficiently small to allow certain experiments to be made.

The first experiments consisted in attempts to obtain the low pressure explosion by means of the "withdrawal" method. In no experiment, either at 513° C. or at 560° C., was the low pressure explosion observed. It was shown that leak of air into the bulb was far too small to cause this result, and also the amount of steam formed during the withdrawal was only large enough to lower the normal explosion pressure very slightly. These experiments confirm the observation of Alyea and Haber* that the reaction chains in the low-pressure region are not initiated on a surface of aluminium (or alumina).

A rough measurement was made of the initial rate of reaction at 513° C. with 200 mm. hydrogen and 100 mm. oxygen; the observed value was of the order 18 mm. pressure change per minute. This rate of reaction is many times larger than the rate in a reaction vessel of porcelain or silica under otherwise similar conditions. Further experiments with aluminium and other vessels are in progress, but it again appears that the surface reaction can only be very indirectly correlated with the low pressure explosion.

Summary.

With the object of investigating possible connections between the heterogeneous combination of hydrogen and oxygen at the surface of silica, and the explosion phenomenon which occurs in silica vessels between certain limits of pressure, the kinetics of this surface reaction have been studied. The rate is nearly independent of the pressure of the oxygen, and is directly proportional to that of the hydrogen.

Thus the active centres are only sparsely covered with hydrogen but are more or less saturated with oxygen. If the theory that the upper explosion limit is determined by a discontinuous change in a layer of adsorbed gas is correct, then this layer is not the hydrogen on the active centres concerned in the surface reaction.

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* 'Z. Phys. Chem.,' B. vol. 10, p. 193 (1930).

Moreover, this theory in any form is rendered very improbable by the fact that excess of either hydrogen or oxygen will prevent the low-pressure explosion, however small the pressure of the other reacting gas may be. The theory of gas phase deactivation at the upper limit is to be preferred. The relative part played by gas and surface in the low-pressure explosion phenomenon is briefly discussed.

It is confirmed that no low-pressure explosion occurs in an aluminium vessel. A vigorous surface reaction occurs however.

We are indebted to the Royal Society, and to Imperial Chemical Industries, Ltd., for grants in aid of this work, and desire to express our thanks to them.

The Atomic Weight of Xenon.

By R. Whytlaw-Gray, F.R.S., H. S. Patterson, and W. Cawood, The University, Leeds.

(Received July 24, 1931.)

The values of 130·2 and 82·9 for the atomic weights of xenon and krypton respectively in the International Table of Atomic Weights* are based on the determinations made by Moore† of the densities of the two gases and on the calculations of Watson of their deviations from the gas laws.‡ The accuracy of these values was first called in question by Aston in 1922, who examined the gases in his early mass spectrograph and deduced from the relative intensities of the lines of the isotopes the figures 131·3 and 83·5.

More recently, using the improved mass spectrograph and a more accurate method of computing intensities,§ he has obtained the values 131·27 ± 0·04 and 83·77 ± 0·02, and since his measurements for other elements, notably mercury, zinc, molybdenum, chromium and tin, give values which accord very closely with the best chemical determinations, it appeared likely that the accepted atomic weights both of xenon and krypton were in error.

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* 'Trans. Chem. Soc.,' p. 1617 (1931).

† 'Trans. Chem. Soc.' (1908).

‡ 'Trans. Chem. Soc.,' p. 833 (1910).

§ 'Proc. Roy. Soc.,' A, vol. 126, p. 511 (1931).

When this work was first planned, no density determinations of either gas had been made for over 20 years, but quite recently the correctness of the mass spectrograph values has been supported by some preliminary density determinations published by Allen and Moore,[*] which lead to the atomic weights Xe = 131·4 and Kr = 83·6, and also by the value Kr = 83·62 obtained by Watson a few months ago.[†] Neither of these determinations lays claim to any final degree of accuracy, and both are to some extent uncertain since no direct measurements of the compressibilities of the gases have been made anywhere near one atmosphere pressure.

At Dr. Aston's suggestion, and in order to see whether the limiting density method would lead to a result in close accordance with that of the mass spectrograph, we undertook to redetermine the atomic weight of xenon. In order to attain an accuracy in the final result of the order of 1 part in 10,000, it was necessary (*a*) to have sufficient gas to fractionate until successive samples showed no change in density, (*b*) to be able to measure the density of a small sample with the requisite precision. Fortunately, a relatively large volume of xenon was available, for Dr. Aston very kindly placed at our disposal 235 c.c. of this precious material, which he had separated from liquid-air residues collected over a long period by the late Sir James Dewar. The use of a special form of microbalance enabled the necessary accuracy to be reached and measurements to be made with only 8 to 9 c.c. of xenon at the highest working pressure.

Method.

Instead of using the classical method for the determination of density, we have compared directly the balancing pressures of oxygen and xenon by means of a sensitive microbalance. The form of the instrument used is the outcome of considerable experience and eliminates many sources of error which hitherto have rendered difficult the attainment of a high degree of accuracy. Various types of buoyancy microbalance have been described in the literature, beginning with the form used by Aston in his early work on the separation of the isotopes of neon.[‡] In this form the beam rests on a central knife-edge, as in the original Steele and Grant instrument. Later Taylor[§] replaced the central knife-edge by a stretched quartz fibre sealed on to the beam, reverting to the principle first employed by Nernst, and he obtained for the densities of oxygen, hydrogen, and helium values comparable in accuracy with those determined by the standard methods, in which the gas is weighed directly. Recently Stock and Ritter* introduced a rather larger balance of the Aston type for high precision work, in which the beam is pivoted on needle points resting in carborundum cups, but it seems to us doubtful whether the accuracy they claim is really attained, since their values for the densities of oxygen and ethylene show considerable variations.

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[*] 'J. Amer. Chem. Soc.,' vol. 52, p. 4173 (1930).

[†] 'Nature,' vol. 127, p. 631 (1931).

[‡] 'Proc. Roy. Soc.,' A, vol. 89, p. 440 (1914).

[§] 'Phys. Rev.,' vol. 10, p. 853 (1917).

The main difficulty with the buoyancy microbalance is to ensure that the zero point remains really constant over long periods. Any form of point or knife-edge has been found to cause minor fluctuations, often difficult to detect, which render the instrument valueless for accurate work.

The form finally adopted utilises the principle of a horizontal fibre suspension and is of such small dimensions that it can be contained in a cylindrical glass tube of about 25 c.c. capacity. It has the further advantage of being compensated, so that the effective surfaces on the two sides of the beam are nearly equal, and hence errors due to adsorption are very largely eliminated. In addition, by suspending the buoyancy bulb by a fibre instead of sealing it directly on to the beam the possibility of a lateral shift of the centre of gravity altering the zero when the gas pressure is changed, is avoided entirely. Moreover, by the addition of small weights to the hook carrying the bulb, the balance can be made to float at a series of densities, and thus the balancing pressures of any two gases can be compared at lower and lower densities and the limiting ratio determined. It may be pointed out, too, that since the method is comparative, a large number of errors inherent in the determination of density in absolute measure vanish, such as any uncertainty in the exact value of the gravity constant, the density of mercury, or the length of the manometric scale. Thus, provided the gases are pure and the zero of the balance constant, determinations of relative density are reduced to the measurement of the length of the manometric column.

The form of the balance is shown in fig. 1.

The balance itself and its supporting frame is made of fused quartz. AA is the beam consisting of silica rod 1 mm. in diameter, swinging between two stretched fibres BB which are fused directly to it at DD. The fibres, which lie as nearly as possible in the same horizontal plane, are fused at their outer ends CC to two vertical rods attached to the frame EE. The latter is made from heavy rod of about 4 mm. diameter and is rectangular in form and arranged so that it will fit easily into the glass tube which serves as a case. Fused to one end of the beam is a vertical quartz fibre carrying a hook, to which is attached the buoyancy bulb H and the small weight K. The bulb is counterpoised by a small fixed weight L and a quartz microscope cover-glass MM, the surface of which has been fused. The cover-glass also serves the purpose of providing a compensation for adsorption, it being so placed that the total surface moments on each side of the beam are nearly equal. The balance is designed for use as a null-point instrument and its zero is defined by a fixed point N attached to the frame in close juxtaposition to a fine pointer O on the end of the beam. The position of the pointer is read by a microscope carrying an eyepiece micrometer.

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* 'Z. Phys. Chem.,' vol. 119, p. 333 (1926) and vol. 124, p. 204 (1926).

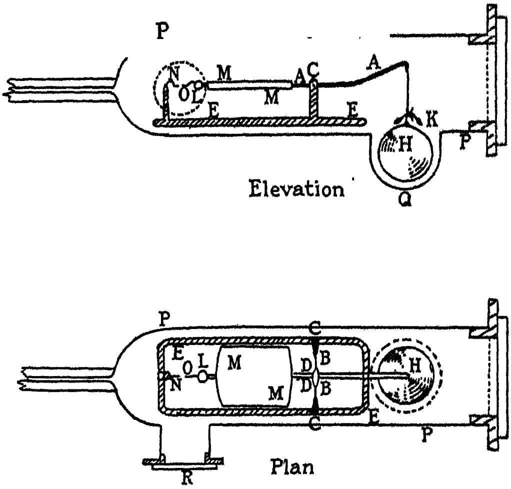

Fig. 1.

The microbalance and frame slides into a cylindrical glass tube PP provided with a projecting depression Q, to take the bulb and a side tube carrying a plate glass window R, through which the pointer can be observed. The case is closed by a plate of ground glass, working on a ground brass collar.

Some care has to be exercised in effecting the compensation for surface of the balance. Equality of surface moments on both sides is first attained approximately by fusing the edges of the cover-glass until its surface, originally too great, is reduced nearly to that of the bulb. The cover-glass is then sealed on to the beam as nearly as possible in the right position, and the latter balanced roughly. This is effected by sealing on two stiff fibres at DD and supporting these on two plane surfaces so that the beam can swing freely, when the subsidiary counterweight L can be adjusted to balance. At this stage an accurate computation of surface moments is made taking L into account, and to effect a final adjustment the edges of the cover-glass are fused again. The balance is then attached to the uprights by fusing on delicate fibre suspensions and finally the centre of gravity of the instrument is adjusted to give the requisite sensitiveness.

The balance we have used carries a buoyancy bulb of a little over 2 c.c. capacity. It will detect a pressure change in oxygen well below 0·01 mm., so that the accuracy of the measurements is determined by the precision with which the pressure can be read. For our manometer we were restricted to tubing of rather narrow bore, on account of the small amount of gas likely to be available after rigorous fractionation, the internal diameter being 11·8 mm. This necessitated a correction for the meniscus height which we were afraid might impair the accuracy of our readings. A practice was always made of measuring the heights of the meniscuses and applying the appropriate capillary correction. We found that, although very considerable variation of meniscus height may occur with one and the same sample of gas, the corrected values of the pressure not only agree extremely closely, but they afford no evidence whatever of dependence on meniscus height.

The actual measurements of the length of the manometric column were referred to a standard glass scale, made by the Société Genevoise, the maximum error of which did not exceed 0·005 mm. on the total length of 1 metre. The lines were diamond ruled, their thickness being of the same order. The positions of the two mercury meniscuses relative to the lines were read by means of a vertical comparator made to our design by the Precision Tool and Instrument Company, Newington Butts, London. This carried two telescopes fitted with micrometers working on standard screw threads, and reading directly to 0·01 mm. The scale and manometer were placed alongside each other in a water bath fitted with plate-glass sides, and were arranged to be in the same focal plane with respect to the telescopes.

Readings were made in the usual way by swinging the comparator column through a small angle. A point of importance is the illumination of the meniscuses. Unless these are carefully shaded by screens placed very close to the surface of the mercury so as to cut out overhead illumination, an error of a few hundredths of a millimetre may easily be made.

The case containing the balance fitted into a heavy brass cube, of side about 14 cm., bored for illumination and thermometers. Between the balance case and the manometer a small tube containing tightly packed gold foil was placed to absorb mercury vapour, the connection being completed by a spiral of fine tubing to prevent the transmission of vibration. The gold tube and spiral were both heavily lagged with cotton-wool.

During the course of the day the temperature gradually rose a few degrees, but the temperature of the manometer and of the balance as a rule changed approximately at the same rate, the manometer rising in temperature rather more slowly. This slow variation in temperature, which at first appeared a doubtful factor, has the advantage that the positions of the two meniscuses slowly alter and pressure readings are never made at the same points in the manometer tubes; any error due to irregular refraction through the glass will, therefore, tend to be annulled in a series of readings.

The temperature of the balance case was read to 0·01° C. in order to correct the readings to any suitable selected temperature.

In practice we have used 18° C., as most of the readings ranged about this value.

The general arrangements of the balance and manometer will be clear from the accompanying diagram.

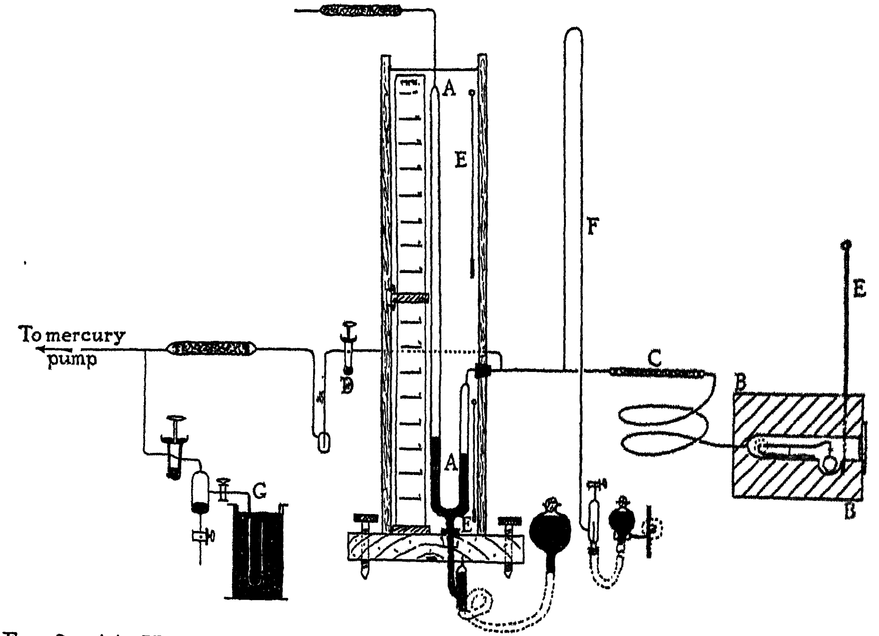

FIG. 2.—AA, Manometer enclosed in water-bath. BB, Block containing microbalance case. C, Gold tube. D, Tap communicating with fractionating vessel and Antropoff pump. EEE, Thermometers. F, Pressure adjuster. G, Syphon for the introduction of gas.

The Course of an Experiment.

In carrying out an experiment it was first necessary to decide for what density the balance should be adjusted. A suitable weight of quartz fibre was then placed on the hook above the buoyancy bulb, and the apparatus evacuated to below 0·01 mm. pressure. Pure oxygen was then introduced until the balance began to swing free from its arrestment. It was next adjusted to its reference point, *i.e.*, to zero, by altering slightly the volume in the system by means of the pressure adjuster. This consisted of a fine capillary tube, the volume of which could be varied by raising or lowering a mercury reservoir working on a rack and pinion.

The whole apparatus was then allowed to attain thermal equilibrium, when a slight further adjustment was usually necessary to bring the balance to the zero point. The readings of pressure and the temperatures of balance case and water-bath were then made.

Though the temperature was usually rising very slowly, the actual variation of pressure during the interval of time necessary for the readings was as a rule beyond the limit of error of the measurements. Any possible error which might have been introduced in this way was eliminated by interposing the readings of one meniscus between two readings of the other. Variations in density too small to be measured on the mercury column were detectable on the balance and occasionally it was necessary to make a small correction for this drift from the zero position.

After a sufficient number of readings had been made with oxygen, the xenon was introduced and the same procedure followed. Since temperature varied somewhat between the two sets of readings they were all reduced to standard conditions, *i.e.*, to 18° C. for the gas pressure expressed in terms of a mercury column at 0° C. For the reduction the coefficient of expansion of oxygen at the appropriate pressure was used, and for xenon we employed the corresponding coefficient for ethylene, since the critical points of xenon and ethylene approximate closely.

It may be noted that no error was introduced into the xenon results in this way, since the correction was only made at most over one or two degrees and, moreover, the pressure of xenon was so low that practically no error would have been caused had it been treated as an ideal gas. In many cases the xenon was removed and the balancing pressure redetermined with oxygen. This served as a check on the constancy of zero of the balance, which proved to be remarkably free from variation; indeed, for weeks on end no change in zero could be detected, and the same specimen of gas always gave the same balancing pressure. To obtain the ratio of the balancing pressures at another density the weight was changed and the same procedure repeated.

The following figures taken at random from our note-book give an example of a typical single pressure reading and the corrections applied.

Oxygen Balancing Pressure.

Pressure readings, in millimetres.		Height of meniscus in millimetres.		Temperature, degrees C.		Pointer of balance.
Lower meniscus.	Upper meniscus.	Lower.	Upper.	Balance.	Bath.	
96·28 96·28	— —	— —	— —	17·56	—	set
— —	426·74 426·74	1·71	1·02	—	17·7	—
96·28 96·28	— —	— —	— —	17·56	—	set

Corrections to pressure—

(1) For meniscus height—

$\left.\begin{array}{l}\text{Upper } +0{\cdot}18 \\ \text{Lower } +0{\cdot}28\end{array}\right\}$ difference .... −0·10

(2) Correction of manometer column from 17·7° C. to 0° C. .... −1·00

(3) Correction of gas pressure from 17·57° C. to 18° C. using coefficient of expansion of oxygen at constant pressure of 330 mm. .... +0·49

$$\text{Corrected pressure} = \left\{\begin{array}{r} 330{\cdot}46 \\ -0{\cdot}10 \\ -1{\cdot}00 \\ +0{\cdot}49 \end{array}\right\} = 329{\cdot}85 \text{ mm.}$$

Purity of the Gases.

The oxygen used in these experiments was made by heating a pure specimen of potassium permanganate in a vacuum. The gas was passed through red-hot copper oxide, then over liquid and solid potash, dried with phosphoric anhydride and finally liquefied.

A large quantity of the liquefied gas was allowed to boil away and the middle fraction collected and stored in glass flasks which had been carefully pumped out. The question of the purity of the oxygen prepared in this way was recently investigated in this laboratory by Dr. M. Woodhead and Dr. F. L. Roberts, who found that its balancing pressure was identical with that of oxygen prepared from potassium chlorate and purified in a similar way. Moreover, after a careful series of tests on both samples, it was concluded that any nitrogen remaining could only be present in quite negligible amounts.

The 235 c.c. of xenon lent by Dr. Aston proved to be remarkably pure, and after condensation in liquid air only a small fraction of a cubic centimetre of less condensable gas could be removed through the mercury pump. The whole of the remaining xenon was then resolidified, pumped off again, and the temperature allowed to rise slowly until the solid exerted a pressure of about 10 mm. At this pressure the gas was collected through the mercury pump, in six approximately equal fractions, and put aside for examination.

The first, last and third fractions were then introduced successively into the balance case and the balancing pressures determined.

In doing this the gas was always solidified in the small vessel next to tap D in fig. 2 and pumped for some minutes before it was allowed to flow into the case. Any small bubbles of gas collected in this way were kept apart in a residue tube. The fractions examined showed clearly a progressive rise in density from the first to the last, but the difference in balancing pressure was small, the extreme variation being 0·18 mm. on a pressure of 153 mm. or about 1 part in 900. It was clear that the gas contained a small amount of a more volatile impurity, which was almost certainly krypton. Since no impurity heavier than xenon could be present, the obvious procedure was to continue fractionation until no further increase of density occurred.

Accordingly fractions 4, 5 and 6 were mixed and fractionated, but this time the pressure was allowed to rise above 600 mm. so as to allow the gas to liquefy. It was thought that by this means a better separation would be effected and also that any air adsorbed by the solid would be eliminated. Five fractions were obtained which still showed a small progressive increase in density, but the balancing pressure of the last agreed very closely with that of fraction 6 in the previous series.

This distillation at high pressure was difficult to carry out with the small quantity of gas at our disposal, and since it did not yield a final material of higher density, recourse was had again to sublimation at low pressure. The five fractions from the previous operation were solidified and sublimed at a low pressure into a second vessel and then pumped off into four fractions. These were examined and it was found that the density of the last fraction had increased slightly and that the small quantity of more volatile substance was accumulating in the first runnings. The same process was therefore repeated using the last two fractions from the previous operation and the density of the last fraction taken, and finally a third sublimation was carried out. By this time the original volume of gas, which was about 110 c.c., had been reduced to about 35 c.c. and the balancing pressure of the last fraction had become constant within the limits of measurement. There seemed to be little doubt that the gas was very pure. As a final precaution and also to get rid of any traces of oxygen, which our experience with xenon some 20 years ago* had shown was difficult to eliminate, the gas was mixed with a few cubic centimetres of pure hydrogen from palladium and sparked for some time in a gas tube over mercury.

The xenon was then condensed once more, the hydrogen removed by pumping and the balancing pressure measured. No alteration in density could be detected. The balancing pressures of the last fraction of the gas after each of the three sublimations and after the sparking with hydrogen are given below. It may be noted that each figure is the mean of a number of separate pressure determinations which agreed very closely with each other after correction to the standard temperature of 18° C.

Balancing pressure of last fractions after the four successive final sublimations.

Fractionation.	Balancing pressure.
(*a*)	152·96
(*b*)	152·94
(*c*)	152·93
(*d*)	152·93 after sparking.

It will be seen from these figures that fractionation was continued until any changes in density lay within the limits of experimental error. We may point out again that any impurity which could possibly be present would be less dense than xenon, and were it less volatile it would tend to accumulate in the last fraction, and the density of this would have been less than the last but one. We obtained no indication whatever of this, indeed the last fraction but one always proved to be rather lighter, by a very small but quite definite amount, which however would have had little influence on the atomic weight.

Throughout all the operations of transference and manipulation the greatest care was taken to exclude contamination by minute traces of air or oxygen. With so dense a gas as xenon it is easy to see that a minute amount only will exert a considerable effect on the balancing pressure, in fact about 0·1 c.mm. of air per cubic centimetre of xenon will cause an alteration of 0·01 mm. at the higher pressure. In dealing with a condensable gas, however, there is no difficulty in ensuring that such a quantity is absent, for the xenon was frozen and pumped down below its vapour pressure each time before it was introduced into the apparatus. Also in changing over from air or oxygen to xenon, the apparatus after evacuation to below 0·01 mm. was always washed out with a little xenon.

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* 'Proc. Roy. Soc.,' A, vol. 86, p. 579 (1912).

Another source of error encountered in the course of the work arose from the slow contamination of the oxygen when allowed to stand in the apparatus after it had been used for xenon.

The balancing pressure was observed to fall gradually by some hundredths of a millimetre and this was traced to the slow evolution of xenon from inside the balance case, probably from the grease used on the terminal plate. Once discovered there was, of course, no great difficulty in avoiding it.

Numerical Results.

The purity of the xenon having been established, the ratios of the balancing pressures of oxygen and xenon were determined with the final sample of gas (*d*). The ratios were measured at two densities corresponding to pressures of xenon of about 153 and 80 mm. The pressures are corrected to a standard temperature of 18° C. and expressed in terms of a mercury column at 0° C.

Density 1.

(Balancing pressures in millimetres.)

Xenon.	Oxygen.	Mean ratio.
152·93	627·81	$\frac{\text{Oxygen pressure.}}{\text{Xenon pressure.}}$
152·94	627·86	
152·94	627·81	
—	627·79	
Mean 152·93(7)	627·82	4·1051

Density 2.

Xenon.	Oxygen.	Mean ratio.
80·39(3)	329·84	$\frac{\text{Oxygen pressure.}}{\text{Xenon pressure.}}$
80·38(1)	329·85	
80·37(5)	329·85	
80·37(2)	—	
Mean 80·38(0)	329·85	4·1036

Before these results can be used for calculating the limiting value of the ratio, a small correction must be applied on account of the variation in volume of the buoyancy bulb with changing pressure.

Thus at density 1 there is a difference in pressure between the oxygen and xenon of 475 mm., and hence the bulb displaces more gas and balances at a lower density in xenon than in oxygen. To calculate, therefore, the true value of the balancing pressure in xenon the latter must be increased by a small amount, *i.e.*, the ratio must be diminished.

We are indebted to Mr. Whitaker for making a careful study of the alteration in volume of a batch of silica bulbs from which our bulb was chosen. The shrinkage was found to be directly proportional to the pressure and to vary little from bulb to bulb. The change per atmosphere was very approximately 2×10^{-4} c.c. As the correction is of the second order it is unnecessary to know it exactly. The corrected ratios at densities (1) and (2) are therefore 4·1049 and 4·1035, and on extrapolating these linearly to zero pressure 4·1020 is obtained for the limiting ratio.

It seems to us fully justifiable to use here a linear extrapolation, in view of the fact that the lowest pressure is only 80 mm. and the compressibility coefficient of xenon is not unduly large at 18° C.

The atomic weight of xenon is accordingly

$$4 \cdot 1020 \times 32 = 131 \cdot 26\ (4).$$

The actual error of measurement, so far as we can assess it, does not appear to exceed $\pm 0 \cdot 01$, rather greater than the error estimated in a preliminary announcement of these results in 'Nature.'*

This result agrees remarkably closely with that found by Dr. Aston, namely, $131 \cdot 27 \pm 0 \cdot 04$. Indeed, the two are identical within the limits of experimental error. The agreement affords a further confirmation of the accuracy with which atomic weights can be determined with the mass spectrograph.

From the two experimental ratios we can calculate the compressibility for xenon at 18° C. in the following way.

Adopting Guye's notation $1 + \lambda = p_0 v_0 / p_1 v_1$, where $p_0 v_0$ and $p_1 v_1$ are the pv values of the same mass of gas at zero pressure and 1 atmosphere respectively, it can be shown that the experimental ratios R_1 and R_2 are related by the expression

$$R_1 \frac{1 + \lambda_{O_2} p^1{}_{O_2}}{1 + \lambda_{Xe} p^1{}_{Xe}} = R_2 \frac{1 + \lambda_{O_2} p^2{}_{O_2}}{1 + \lambda_{Xe} p^2{}_{Xe}}$$

in which $1 + \lambda_{O_2}$ and $1 + \lambda_{Xe}$ are the compressibilities for oxygen and xenon, and $p^1{}_{O_2}$, $p^1{}_{Xe}$, $p^2{}_{O_2}$, $p^2{}_{Xe}$ the balancing pressures expressed in atmospheres of the two gases corresponding to the ratios R_1 and R_2.

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* Vol. 127, p. 970 (1931).

It is clear that the coefficient of oxygen must be known before that of xenon can be deduced. Unfortunately, $1 + \lambda$ for oxygen is only known exactly at 0° C. It has also been calculated at this temperature from high-pressure data by Beatty and Bridgeman,* who obtained 1·00101, whilst the most probable experimental value is 1·00094, Wild.† Using the Beatty-Bridgeman equation, we have calculated the value for 18° C., which is 1·00081, and if now we assume that the ratio of the calculated to the experimental value is the same at 18° C. as at 0° C., we obtain for $1 + \lambda$ at 18° C. the value 1·00075.

Substituting this figure for oxygen in the above equation, we get for $1 + \lambda$ for xenon at this temperature 1·0068 (0). Although we have every confidence in the accuracy of the atomic weight, we do not feel that great reliance is to be placed on this value, on account of the very short range of pressure over which the measurements were made.

We wish to express our thanks to Dr. Aston for the loan of the xenon and to Imperial Chemical Industries, Ltd., for a grant from which most of the apparatus was purchased.

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* 'J. Amer. Chem. Soc.,' vol. 50, p. 3151 (1928).

† 'Phil. Mag.,' July, 1931.

The Diffusion of Colloidal Electrolytes and Other Charged Colloids.

By G. S. Hartley and Conmar Robinson, University College, London, and Imperial Chemical Industries, Ltd.

(Communicated by F. G. Donnan, F.R.S.—Received July 25, 1931.)

Introduction.

Measurements of the diffusion of colloidal substances have frequently been used as a method for determining their particle size. The well-known Stokes-Einstein equation has generally been considered to give the relationship between the quantities. The influence of electrical forces in making the Stokes-Einstein equation inapplicable seems to have been almost generally neglected. Thus a considerable amount of work has been done on the diffusion of dyes* and conclusions drawn using this equation about the particle size which, as shown in this paper, are quite unjustified. From such work a theory of dyeing with cotton substantive dyes has been built up. Freundlich† in his text book points out that since dyes are electrolytes, the Nernst relation between the diffusion constant and the mobilities of the two ions composing the electrolyte,

$$\frac{1}{D} = \frac{1}{2RT}\left(\frac{1}{U} + \frac{1}{V}\right), \qquad (1)$$

must be taken into account. He then adds, "We can, however, conclude from these measurements at what size of particle, at what value of diffusion constant therefore, a dissolved substance begins to behave like a colloid." He does not, however, point out that this equation only applies to uni-univalent electrolytes. When the extended equation for multivalent electrolytes is used, then, as will be shown later, one cannot conclude even qualitatively what the particle size is.

With the exception of Svedberg‡ and Tiselius,§ who take the electrical forces into consideration in the case of sedimentation equilibrium, previous writers seem for the most part to have entirely neglected the matter. Thus the question is not dealt with at all in the 60 pages devoted to diffusion in von Hahn's "Dispersoidanalyse." Freundlich (*loc. cit.*) goes so far as to say, "Perhaps no method is more fruitful for the investigation of lyophilic sols than the measurement of diffusion . . . the only difficulty is that the measurements are tedious." But, as we will explain, the electrical forces may also play a part in the diffusion of charged colloids not usually considered as "colloidal electrolytes" and give rise to unexpectedly high diffusion velocities. Since the time of Thomas Graham, low diffusion has been considered a characteristic of a colloid, and the possibility of a substance of several thousand "particle weight" having a diffusion coefficient of the same order as that of, for example, copper sulphate does not seem to have been realised. In this respect the recent striking experiments of Bruins* on the diffusion of starch and gum arabic, as well as measurements of diffusion coefficients of dyes by one of us (C.R.), are of considerable interest.

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* Herzog and Polotzky, 'Z. Phys. Chem.,' vol. 87, p. 449 (1914), 'Z. Elektrochem.,' vol. 17, p. 679 (1911), and 'Kolloid Z.,' vol. 2, p. 1 (1907); Haller, 'Kolloid Z.,' vol. 11, p. 110 (1912), vol. 13, p. 255 (1913), vol. 20, p. 127 (1917), and vol. 23, p. 100 (1918); Haller and Nowak, 'Kolloid. Beih.,' vol. 13, p. 61 (1920); Auerbach, 'Kolloid Z.,' vol. 29, p. 190 (1921); Traube and Shikata, 'Kolloid Z.,' vol. 32, p. 313 (1923); Ruggli and Fischli, 'Helv. Chim. Acta,' vol. 7, p. 1013 (1924); Ruggli and Pestalozzi, 'Helv. Chim. Acta,' vol. 9, p. 364 (1926); Nistler, 'Kolloid. Beih.,' vol. 31, p. 1 (1930).

† "Colloid and Capillary Chemistry," London, 1926, p. 533.

‡ 'Kolloid Z.,' vol. 36, Ergänzungsband, p. 62 (1925).

§ 'Z. Phys. Chem.,' vol. 124, p. 449 (1926).

The Diffusion of Multivalent Electrolytes.

Nernst† and Einstein‡ considered the solute contained in a unit volume of solution to behave as though it were acted on by a force equal to the gradient of osmotic pressure. For a discussion of this assumption the reader is referred to a previous publication§ by one of us in which an attempt is made to extend the Nernst theory to finite concentrations of multivalent strong electrolytes. The extension of the Nernst formula to

$$D = RT\left(\frac{1}{n_+} + \frac{1}{n_-}\right)\frac{UV}{U+V}, \tag{2}$$

where the electrolyte gives rise to ions of charge n_+ and n_-, was first published by Haskell,|| who attributes its derivation to A. A. Noyes. In terms of equivalent conductivity in place of absolute mobility this equation becomes

$$D = \frac{RT}{F^2} \,.\, 10^{-7}\left(\frac{1}{n_+} + \frac{1}{n_-}\right)\frac{uv}{u+v}, \tag{3}$$

where F is the equivalent of electricity in coulombs. The value of the constant $\frac{RT}{F^2} \,.\, 10^{-7}$ for 20° C. is $2 \cdot 62 \times 10^{-7}$.

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* 'Kolloid Z.,' vol. 54, pp. 265, 272 (1931).

† 'Z. Phys. Chem.,' vol. 2, p. 613 (1888).

‡ 'Z. Elektrochemie,' vol. 14, p. 235 (1908).

§ 'Phil. Mag.,' vol. 12, p. 473 (1931).

|| 'Phys. Rev.,' vol. 27, p. 145 (1908).

Although the treatment is applicable to all types of colloidal electrolytes, we shall for simplicity confine our attention to a dyestuff, NaR, that is the sodium salt of an organic acid, whose anions form colloidal particles. The substance may be regarded as dissociating as follows

$$n\,\mathrm{NaR} \rightleftharpoons n\,\mathrm{Na}^{+} + \mathrm{R}_n^{n-}$$

if no sodium is included in the anion complex. In this case n_- of equation (2) will be equal to n, but this will not be the case when Na enters into the anion. If the dyestuff is the salt of a dibasic acid, R will denote half of the acid radicle, but it is unnecessary to treat such a case separately if it be borne in mind that n must then be an even number, or a multiple of three for a tribasic acid, etc. In equation (3) the term $(1 + (1/n_-))$ will *decrease* from 2 to 1 as n_- *increases*. Any other change in the value of D with increasing degree of aggregation will be due to the change in the value of $uv/(u + v)$ with change of v. Given a certain value for the mobility of the simple anion R there is every reason to expect that the mobility V of R_n^{n-}, the complex ion, will increase and not decrease with increasing aggregation, since the more complex ion containing the same number of charges as the sum of the constituent ions will offer less resistance to the motion than do the single ions. Consequently $uv/(u + v)$ will increase with increasing aggregation of the anions. We may therefore have cases where the diffusion coefficient increases with increasing aggregation, while the Stokes-Einstein equation would lead us to expect a decrease with increasing aggregation.

The value of v in the case of ordinary electrolytes can be obtained by subtracting the value of u from the equivalent conductivity at infinite dilution. For colloidal electrolytes the relation may not be so simple on account of the possible inclusion of sodium ions in the complex anion. The equivalent conductivity of any electrolyte at any concentration is defined as the specific conductivity of the solution divided by its concentration in gram equivalents per cubic centimetre. In the case of a simple completely dissociated electrolyte, this is equal to the sum of the ion conductivities $u + v$. Where, however, the electrolyte is not completely dissociated or where some of the cation is included in a complex anion, not all the total number of equivalents of metallic or acid radicle are taking part in the conduction of electricity. In order to obtain the sum of the ion conductivities we must divide the specific conductivity not by the chemical equivalent concentration, but by the concentration of mobile electricity in equivalents per cubic centimetre. The two cases are only the same for a completely dissociated electrolyte.

If we assume in the case of the substance NaR that a fraction f only of Na is in the form of the free ion, then the number of equivalents of mobile electricity is equal to f times the number of chemical equivalents, whence the sum of the ion conductivities is given by λ/f where λ is the equivalent conductivity as defined above. Since u is known, we may therefore express the relationship by

$$v = \frac{\lambda}{f} - u. \tag{4}$$

When an electrolyte conducts electricity, the ions must necessarily move in opposite directions. The inter-ionic forces then operate, according to the reasoning of Debye and Hückel, as an additional viscous drag on their motion, increasing as the square root of the concentration. In a diffusing electrolyte the ions necessarily move at equivalent rates in the same direction and these forces do not therefore operate in this way. If we are dealing with conductivity, we find therefore a falling off of the mobility with increasing concentration, which has no counterpart in the case of diffusion.* We must, therefore, employ in the diffusion equation values for u and λ higher than those obtained from conductivity measurements. The appropriate value of u will be that at infinite dilution, u_∞, but that of λ may not be the value at infinite dilution, λ_∞, as the constitution of the anion may change with concentration. We must therefore use a quantity, λ', which will be greater than λ by an amount depending on the influence of the inter-ionic forces on the conductivity, the magnitude of which influence in the case of colloidal electrolytes is very uncertain, but will probably not be large in solutions so dilute as those generally used. Equation (5) now becomes

$$\mathrm{D} = \frac{\mathrm{RT}}{\mathrm{F}^2} 10^{-7} \left(1 + \frac{1}{n_-}\right) \frac{u\left(\dfrac{\lambda'}{f} - u\right)}{\dfrac{\lambda'}{f}} \tag{5}$$

$$= \frac{\mathrm{RT}}{\mathrm{F}^2} 10^{-7} \left(1 + \frac{1}{n_-}\right) \frac{u\,(\lambda' - fu)}{\lambda'}. \tag{6}$$

Since $(1 + (1/n_-))$ cannot be < 1 nor $\lambda' < \lambda$, nor $f > 1$, D cannot be

$$< \frac{\mathrm{RT}}{\mathrm{F}^2}\, 10^{-7} \frac{u\,(\lambda - u)}{u},$$

which is half the value calculated from λ assuming the anion to be simple and univalent. Hence for a high value of λ, D must always be high. The importance of this conclusion will be realised when it is pointed out that in the several cases where the value of λ has been determined for dye solutions, it has been found to be high. In Table I we give the values of λ for several benzidine dyes, together with values for D as obtained by one of us (C.R.) for the purified dyes, as well as values given by other workers.

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* Hartley, 'Phil. Mag.,' vol. 12, p. 473 (1931).

Table I.

	λ_∞ 25°.	λ 1/32 per cent. 25°.	Minimum theoretical.	$D_{18} \times 10^6$.	
				Observed (pure dye).	Previously published.
Congo red	—	90[*]	5·1	5·9[**]	Extremely small[§]
Benzopurpurine 4B	98[†]	90	5·6	4·6[**]	Small[‖]
"Meta" benzopurpurine	92[†]	89	5·2	5·7[**]	—
Bordeaux extra	79[‡]	—	4·0	—	—
Congo rubin	93[**]	90	5·2	5·5[**]	1·86[¶]

[*] Donnan and Harris, 'J. Chem. Soc.,' vol. 99, p. 1554 (1911).
[†] Robinson and Mills, 'Proc. Roy. Soc.,' A, vol. 131, pp. 576, 596 (1931).
[‡] Meier, 'Diss.,' Göttingen (1925).
[§] Herzog and Polotsky, 'Z. Phys. Chem.,' vol. 87, p. 449 (1914).
[‖] Auerbach, 'Koll. Z.,' vol. 29, p. 191 (1921); Schuleman, 'Biochem. Z.,' vol. 80, p. 1 (1916).
[¶] Nistler, 'Kolloid. Beih.,' vol. 31, p. 1 (1930).
[**] Robinson (to be published later).

The value of λ does not vary greatly with concentration for these dyes, consequently λ′ is of the same order as λ_∞. The minimum theoretical values are calculated from the expression

$$\frac{RT}{F^2} 10^{-7} \frac{u(\lambda - u)}{u}.$$

The fact that benzopurpurine 4B gives a lower result than the meta benzopurpurine, although on this theory we should expect the contrary, is possibly due to the higher content of electrolyte impurity indicated by the higher conductivity of the ultrafiltrate.[††] The enormous effect of added electrolytes will be dealt with later (p. 26).

The value of D for N/10 $CuSO_4$ is $4 \cdot 6 \times 10^{-6}$[‡‡] at 18° C. The results on the pure dyes are all higher than this. The "particle weight" of the two benzopurpurines is at least several thousand.[††]

Let us consider the case of two dyes similar to those described by Robinson and Mills[††] whose conductivities are approximately equal and one of which is more aggregated than the other.

[††] Robinson and Mills, 'Proc. Roy. Soc.,' A, vol. 131, pp. 576, 596 (1931).

[‡‡] Thovert, 'Ann. Physique,' vol. 2, p. 405 (1914).

Since n is in both cases large, and hence the valency factor $(1 + (1/n_-))$ not very different, and since λ and u are the same in both cases, it follows that any great change in D must be attributed to change in f. The more complex anion would, as shown above, be expected to have the higher mobility. Association of several simpler anions to form a more complex one can only be reconciled with a constant value of λ by assuming it to be accompanied by inclusion of a greater proportion of the Na^+ ions in the anions, thereby diminishing the increase of v and reducing the contribution made by the Na^+ ions to the conductivity. Increased hydration would also diminish the increase of v, but it is unlikely that it could compensate entirely for the decreased resistance consequent on association of ions (*e.g.*, if 10 ions fuse into one more complex one we should, if f remains constant, expect a mobility $10^{2/3}$ times as great. In order that this increase should be entirely compensated by hydration, we must assume that the radius of the complex anion is increased to $10^{2/3}$ times its unhydrated value by water molecules, *i.e.*, that association of the 10 ions must be accompanied by the attraction of 100 times their volume of water). It is therefore extremely probable that the value of f will be considerably less in the case of the more highly aggregated substance, which leads to the remarkable conclusion that the velocity of diffusion may actually be higher for this substance than for the one whose colloidal particles are very much smaller.

In the formula for the diffusion of an electrolyte at finite concentration which one of us (G.S.H.) has put forward,* the factor $d\ln a_\pm / d\ln C$ appears, where $a_\pm$ is the mean activity and C is the concentration. So far we have not referred to the possible influence of this in the case of dyes. Where the activity coefficient falls greatly with increasing concentration this factor may be of considerable importance. It is quite possible that the activity coefficient of dyes of the type here considered may be low, but, on the other hand, there is no reason to expect that it will be as low as that of an ordinary electrolyte of high valency type. Thus McBain† has pointed out in the case of soap solutions that for a micelle made up of carbon chains 20 Å. long, the distance between the individual charges will be of the same order as the mean distance between the chlorine ions in a 1N NaCl solution, so that we have no condensation of charge.

Preliminary experiments (to be published later) have given values of D, which are high enough to be accounted for without attributing any great influence to this activity factor (lower results obtained by other workers will be referred to when discussing the influence of electrolytes on the diffusion coefficient), and since we have at present no data that would allow us to calculate the activity coefficient with any reliability, it seems at present fruitless to discuss this further. It should, however, be kept in mind as possibly having a considerable influence in at least some cases. The main fact, however, that we cannot deduce anything about the radius of the complex anion from measurements of the diffusion coefficient of the pure dye alone remains unaltered.

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* 'Phil. Mag.,' vol. 12, p. 473 (1931).

† 'J. Am. Chem. Soc.,' vol. 50, p. 1636 (1928).

The Influence of added Electrolytes.

The high values predicted by the Nernst theory for the diffusion velocity of colloidal electrolytes, compared with that of uncharged colloids, are due to the considerable potential gradient set up by the presence of more mobile ions of charge opposite to that of the micelles. If electrolytes other than the diffusing ones are present in a system they provide a medium of higher conductivity than the pure solvent, thereby reducing the potential gradient further and resulting in a lower diffusion coefficient. Further, in this case it is no longer a necessary condition that the two ions diffuse at equivalent rates, since the condition of electrical neutrality can be maintained by diffusion of the other ions present. Accordance with the Stokes-Einstein equation will therefore be approached in the presence of considerable excess of added electrolytes.

The effect of addition of an electrolyte with common ion at uniform concentration in reducing the liquid junction potential of a concentration cell was considered by Abegg and Bose in 1899.* These authors pointed out that this must be accompanied by a change in diffusion velocity, and showed experimentally that the addition of a salt with common ion considerably increased the velocity of diffusion of acids and alkalies. A similar effect had previously been predicted by Arrhenius.† The influence of electrolytes on the potential gradient of colloid systems has been dealt with by Tiselius‡ in connection with sedimentation equilibrium. A quantitative treatment, however, does not seem to have been given.

The effect of added electrolyte is a perfectly general one and the calculation would not be appreciably simplified by confining our attention to the common ion case. Consider an electrolyte whose ions have equivalent conductivities u and v and valencies n_+ and n_- and in which a concentration gradient dC/dh

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* 'Z. Phys. Chem.,' vol. 30, p. 545 (1899).

† 'Z. Phys. Chem.,' vol. 10, p. 71 (1892).

‡ 'Z. Phys. Chem.,' vol. 124, p. 449 (1924).

produces diffusion. The concentration gradient can be considered replaced, as far as diffusion is concerned, by a pressure on the solute content of unit volume equal to the gradient of osmotic pressure. The gradient of osmotic pressure of each ion is proportional to its molal, not its equivalent, concentration gradient. In addition there will act on the cation and anion content of unit volume forces given by the product of the equivalent concentration, the equivalent of electricity F, and the potential gradient, $d\mathrm{E}/dh$. The rates of transfer of the two ions in equivalents per centimetre per second will therefore be given by the following expressions :—

$$\mathrm{G}_{+} = \left(-\frac{\mathrm{RT}}{n_{+}}\frac{d\mathrm{C}}{dh} - \mathrm{F}\frac{d\mathrm{E}}{dh}10^{7}\,.\,\mathrm{C}\right).\frac{u}{\mathrm{F}^2}.10^{-7}, \tag{7}$$

$$\mathrm{G}_{-} = \left(-\frac{\mathrm{RT}}{n_{-}}\frac{d\mathrm{C}}{dh} + \mathrm{F}\frac{d\mathrm{E}}{dh}10^{7}\,.\,\mathrm{C}\right).\frac{v}{\mathrm{F}^2}.10^{-7}. \tag{8}$$

The condition of electrical neutrality demands that these rates be equal, and by Fick's equation, both are equal to $-\mathrm{D}\,.\,d\mathrm{C}/dh$, whence we obtain the formula previously quoted (3). If now we introduce another electrolyte, whose ions have conductivities u' and v', at uniform concentration, C', its ions will be, initially, acted on by the electrical force only, whence we shall have for their equivalent rates of transfer

$$\mathrm{G}_{+}' = -\mathrm{F}\frac{d\mathrm{E}}{dh}.10^{7}.\mathrm{C}'.\frac{u'}{\mathrm{F}^2}.10^{-7}, \tag{9}$$

$$\mathrm{G}_{-}' = +\mathrm{F}\frac{d\mathrm{E}}{dh}.10^{7}.\mathrm{C}'.\frac{v'}{\mathrm{F}^2}.10^{-7}. \tag{10}$$

The condition of electrical neutrality now demands that

$$\mathrm{G}_{+} + \mathrm{G}_{+}' = \mathrm{G}_{-} + \mathrm{G}_{-}';$$

and, if we are measuring the diffusion of the anion (*e.g.*, diffusion of dyestuff followed colorimetrically), we must write, by Fick's equation,

$$\mathrm{G}_{-} = -\mathrm{D}\,d\mathrm{C}/dh,$$

whence we obtain

$$\mathrm{D} = \frac{\mathrm{RT}}{\mathrm{F}^2}.10^{-7}.\frac{v}{n_{-}}\left[1 - n_{-}\frac{\dfrac{v}{n_{-}} - \dfrac{u}{n_{+}}}{u + v + \dfrac{\mathrm{C}'}{\mathrm{C}}(u' + v')}\right]. \tag{11}$$

This reduces, of course, to the previous formula for $\mathrm{C}' = 0$, and, for C' very great with respect to C, it becomes

$$\mathrm{D} = \frac{\mathrm{RT}}{\mathrm{F}^2}.10^{-7}.\frac{v}{n_{-}}, \tag{12}$$

i.e., in the presence of large excess of another electrolyte at uniform concentration, the ions of the "diffusing" electrolyte move independently, at rates determined only by their own mobilities.

Since G_+, G_- will be in general unequal and G_+', G_-' not zero, it follows that the concentration gradients of the ions of the colloidal electrolyte will not remain equal and that concentration gradients of the ions of the non-diffusing electrolyte will be built up. The equations (7), (8), (9) and (10) will therefore be strictly true only at the commencement of diffusion and will become increasingly less strictly valid with lapse of time. Equation (11) also is therefore true only at the commencement of diffusion. When C′ is very large compared with C the effect of time will become negligible and the limiting equation (12) will therefore remain valid.

In the presence of great excess of added electrolyte at uniform concentration, the total ionic strength will be approximately constant throughout the solution and therefore the activity factor $d\ln a/d\ln C$ will vanish, being equal to unity, since the activity of an ion is approximately proportional to its concentration in solutions of the same total ionic strength.

We suggest that, when it is practicable, the measurement of diffusion velocity in the presence of great excess of added electrolyte at uniform concentration will be a valuable method of determining particle size. Under these circumstances, the effect of potential gradient being eliminated, we can apply the Stokes-Einstein equation to relate particle size and diffusion velocity.

Measurements by one of us have shown that the diffusion velocity of "meta" benzopurpurine, at a concentration of about 1/32 per cent., is reduced to about half the value of the pure dye when it takes place in 1/250 N NaCl, and to a limiting value of about quarter that of pure dye in N/10 NaCl solution.

This effect of added electrolyte suggests that the presence of traces of other electrolyte as impurity may account for the low values that have sometimes been obtained for the diffusion velocities of dyestuffs.

If another electrolyte is present as an impurity, we should, at the commencement of diffusion, have a concentration gradient in its ions proportional to that of the dyestuff itself. Let the number of equivalents of impurity be x times the number of equivalents of dyestuffs, then we shall have equation (7) and (8) as before, but in place of (9) and (10) we shall have, assuming the added electrolyte to be uni-univalent,

$$G_+' = \left[-RTx \, . \, \frac{dC}{dh} - F\,\frac{dE}{dh} \, . \, 10^7\,Cx\right]\frac{u'}{F^2} \, . \, 10^{-7}, \qquad (13)$$

$$G_-' = \left[-RTx \, . \, \frac{dC}{dh} + F\,\frac{dE}{dh} \, . \, 10^7\,Cx\right]\frac{v'}{F^2} \, . \, 10^{-7}. \qquad (14)$$

Eliminating $d\mathrm{E}/dh$ as before, we obtain

$$\mathrm{D} = \frac{\mathrm{RT}}{\mathrm{F}^2} \cdot 10^{-7} \cdot \frac{v}{n_-} \left[1 - n_- \frac{\dfrac{v}{n_-} - \dfrac{u}{n_+} + x\,(v' - u')}{u + v + x\,(v' + u')} \right]. \tag{15}$$

This differs from equation (11) in that it does not approach the limit

$$-\frac{\mathrm{RT}}{\mathrm{F}^2} \cdot 10^{-7} \cdot \frac{v}{n_-}$$

for great values of x, and, if $v' - u'$ is opposite in sign to $v/n_- - u/n_+$, as it would be for the case of NaCl as an impurity in a dyestuff, the factor in the square brackets might become negative for large values of x, *i.e.*, the diffusion of dyestuff would be inhibited or even reversed.

As before, however, the equations are valid only at the commencement of diffusion, and the effect of time will be greater in this case than in the uniform concentration case, because we are in general dealing with smaller concentrations of added electrolyte. It is interesting, however, to calculate the values given by equation (15) in order to get an idea of the magnitude of the error that would be caused by impurity. For the case of a sodium dye, when equivalent conductance at 18° C. is 86, and in which the anion carries ten charges and no sodium ions, *i.e.*, $u = v = 43$, $n_+ = 1$, $n_- = 10$, we obtain for $x = 0$ the value $\mathrm{D} = 6{\cdot}15 \times 10^{-6}$ and for $x = 0{\cdot}67$, which corresponds to 10 per cent. of impurity if this be NaCl and the equivalent weight of the dye be 350, $\mathrm{D} = 3{\cdot}29 \times 10^{-6}$, *i.e.*, if the dye used were only 90 per cent. pure, the diffusion coefficient would be little more than half that of the pure dye.

It is clear from this example that purity of material is extremely important. It is possible, therefore, that impurity accounts for many of the low results previously published, such as those quoted in Table I. Lower values than would be expected have been quoted, for example, for Congo red, whereas measurements made by one of us on this substance purified by the method described in a previous paper* have given a value of $5{\cdot}9 \times 10^{-6}$.

The Diffusion of Charged Colloids not generally treated as Electrolytes.

The influence of the electrical forces on the diffusion coefficient must also be taken into account in those cases not generally treated as colloidal electrolytes where we have a charged particle accompanied by osmotically active ions of opposite charge. Whether the charge is due to the dissociation of some ionogenic group in the micelle itself or whether it is due to strong selective adsorption of one of the ions of a " foreign " electrolyte is immaterial for the purpose of this theory. For this treatment it is more convenient to give the equation for the diffusion coefficient in terms of particle size rather than in terms of conductivity.

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* C. Robinson and H. A. T. Mills, 'Proc. Roy. Soc.,' A, vol. 131, p. 576 (1931).

If we assume Stokes law to be valid, the mobility V is connected with valency and anion radius by

$$V = \frac{1}{6\pi\eta N} \cdot \frac{n_-}{r_-} \tag{16}$$

where η is the viscosity and N the Avogadro constant. A similar expression holds good for U. Introducing these values into equation (2) we obtain

$$D = \frac{RT}{6\pi\eta N} \cdot \frac{n_+ + n_-}{n_+ r_- + n_- r_+}. \tag{17}$$

This is the counterpart of the Einstein equation when the electrical charge of the colloid is taken into consideration. The equation is identical with that deduced by Svedberg,* who also pointed out that the origin of the charge is immaterial. The significance of the equation has, however, it seems, not been generally realised.

Substitution of (16) in (12) gives the limit for D_{anion} for a large excess of added electrolyte as

$$= \frac{RT}{6\pi\eta N} \cdot \frac{1}{r_-}, \tag{18}$$

which is the well-known Einstein equation, this being here valid since the potential gradient has been eliminated.

The value of D given by (17) reduces to (18) also for the case of $n_- = 0$, *i.e.*, for the case of an uncharged colloid particle.

As will be shown by specific examples using these formulæ, the presence of a charge on the particle accompanied by osmotically active ions of opposite charge can therefore give rise to a diffusion velocity several times that of the uncharged particle. We suggest that this is the explanation of the unexpectedly high values of the diffusion coefficient sometimes obtained for colloids. The recent interesting measurements of Bruins, who found not only unexpectedly high diffusion coefficients for solutions of starch and gum arabic, but that these diffusion coefficients fell to a fraction of their original value on the addition of electrolytes, seems to be an example of this. Unfortunately, we have no figures that would give us the particle size and the charge for the solutions actually used in these experiments. However, by taking possible figures deduced from osmotic pressure and conductivity measurements on other solutions, it is possible to predict diffusion coefficients of the order he obtained and to show that these would fall to about one-fifth of their original value on the addition of electrolytes.

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* Svedberg, 'Kolloid Z.,' vol. 36, Ergänzungsband, p. 62 (1925).

Samec and von Hoefft found osmotic pressure for starch solutions corresponding to a molecular weight of 100,000.* Such a figure would be more likely to be low than high, as the pressure would probably be in part due to osmotically active ions. Let us assume a particle radius of $r_- = 4 \times 10^{-7}$ cm. The "molecular weight" of the particle is given by $M = \frac{4}{3}\pi r_-^3 \rho N$ where ρ is the density of the colloid substance. In the case of starch or gum arabic, where the density is not much greater than water, M = about 180,000 for the value of r_- taken. Figures for the corresponding particle size of gum arabic are not available, but it might be expected to be of this order or larger.

Substituting this value of r_- in equation (18) we get

$$D = 0 \cdot 53 \times 10^{-6}$$

which is the diffusion coefficient of the *uncharged* particles.

If we assume that the particle carries n_- charges and that the electrical neutrality of the system is made up by n_- free Na ions whose radius calculated from mobility is $1 \cdot 8 \times 10^{-8}$ cm., we obtain from (20) at 20° C.

$$D = 2 \cdot 12 \times 10^{-13} \frac{1 + n_-}{4 \times 10^{-7} + 1 \cdot 8 \times 10^{-8} \times n_-}$$

$$= 2 \cdot 12 \times 10^{-6} \frac{1 + n_-}{4 + 0 \cdot 18 n_-}, \tag{19}$$

for $n_- = 5$, $D = 2 \cdot 5 \times 10^{-6}$.

The presence of a charge of 5 on the particle of 180,000 molecular weight is therefore sufficient to raise the value of D five times.

It remains to justify the assumption of such a charge and to show that the fall of D could be brought about by the small amounts of electrolytes added in Bruins' experiments.

For a given radius of particle and a given value for n_- we may calculate the equivalent conductivity of the particle from equation (16) assuming Stokes' law. Some figures for the case of $r_- = 4 \times 10^{-7}$ cm. are given in the following table as well as the values for D obtained from (19).

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* 'Kolloid. Beih,' vol. 5, p. 195 (1913).

Table II.

n_-.	D at 20° C.	v_{18}.	λ_{18}.	Specific conductivity of 1 per cent. solution at 18° C.
0	$0\cdot53 \times 10^{-6}$	0	—	0
1	$1\cdot01 \times 10^{-6}$	2	45	$2\cdot5 \times 10^{-6}$
3	$1\cdot87 \times 10^{-6}$	6	49	$7\cdot8 \times 10^{-6}$
5	$2\cdot50 \times 10^{-6}$	10	53	$14\cdot7 \times 10^{-6}$
10	$4\cdot02 \times 10^{-6}$	20	63	$35\cdot0 \times 10^{-6}$

In obtaining the figure of 4×10^{-7} cm. for the radius of the particle we have neglected any influence of hydration. The hydration of such sols is generally assumed to be very high. Supposing it was great enough to increase the effective volume of the particle by three times, r_- would then be $5\cdot77 \times 10^{-7}$ cm. and for $n_- = 0$, D would be $0\cdot37 \times 10^{-6}$, while for $n_- = 5$, D would be $1\cdot90 \times 10^{-6}$, and the specific conductivity would be $13\cdot9 \times 10^{-6}$, so that here the effect of the charge is somewhat greater.

Conductivity measurements made by us on a 2 per cent. solution of " Turkey Elect " gum arabic at 18° C. showed the specific conductivity to be initially as high as $1\cdot7 \times 10^{-4}$. The solution was dialysed in a collodion thimble, with frequent changes of water. At the end of a week the specific conductivity had fallen to 9×10^{-5}. Dialysis was then apparently complete. It is probable therefore that the specific conductivity for " pure " gum arabic will be at least as high as 5×10^{-5}, which is considerably more than any of the figures given above. A 1 per cent. solution of soluble potato starch had a steady specific conductivity of $1\cdot25 \times 10^{-5}$, after similar treatment, while a $0\cdot8$ per cent. solution of ordinary wheat starch had a high conductivity before dialysis, namely, $1\cdot5 \times 10^{-5}$, which fell to a final value of $0\cdot5 \times 10^{-5}$. This last value is too low to fit in with figures of the order of those given above. However, the sols used by Bruins were not subjected to any method of purification such as dialysis, and the conductivity of the solutions actually used would consequently be almost certainly considerably higher than this. Even if the conductivity could be considerably reduced by dialysis, it might not be due to additional electrolyte in the sense of this theory—the electrolyte removed might have been strongly selectively adsorbed and so contributing to a considerable charge on the particle. Bruins mentions neutralising the slightly acid gum arabic with caustic soda.

If we take the particular case where the particle has a radius of 4×10^{-7} cm. and a charge of 5, which gives $D = 2\cdot5 \times 10^{-6}$, it is possible, using equation

(11) to calculate what would be the corresponding diffusion coefficient in the presence of 1 and 20 m-equivalent of KCl per litre respectively where the concentration of the substance considered is 0·6 per cent. (*i.e.*, a concentration 1/6 m-equivalent per litre). These results are given in Table III, together with the values for D obtained by Bruins for two specimens of gum arabic and one of starch.

Table III.

KCl (in m-equivalent).	Diffusion coefficient $\times 10^6$.			
	$n_- = 5$ $r_- = 4 \times 10^{-7}$.	Gum arabic.		Starch III.
		A.	B.	
0	2·5	2·5	2·2	1·3
1	0·64	0·8	0·58	0·4
20	0·53	—	0·32	—
∞	0·53	—	—	—

We find, therefore, that not only can a very great fall of the diffusion coefficients of such substances be accounted for, but that 1 m-equivalent of KCl per litre could bring about the greater part of this fall, as was found experimentally.

Further, in referring to two other starch sols that were studied, Bruins remarks that the drop in D was found to be greatest in the case where the diffusion coefficient was greatest. This is what we would expect. The diffusion coefficients were as follows :—

	$D \times 10^6$
Starch I	0·24
„ II	1·0
„ III	1·3

Starch III was probably the purest, starch I already containing sufficient electrolyte as impurity to bring about a considerable part of the lowering.

The phenomenon will, of course, not be confined to lyophilic sols. In those cases, *e.g.*, the lyophobic gold sols studied by Westgren* and Svedberg† where values of the right order were obtained for the Avogadro constant by means of the Stokes-Einstein equation, it seems that sufficient electrolyte may have been present to make the influence of the electric forces negligible, the amount of electrolyte necessary for this being small owing to the very high "equivalent" of the colloid.

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* Westgren, 'Z. Phys. Chem.,' vol. 89, p. 63 (1914).

† Svedberg, "Die Existenz der Moleküle," p. 78.

Summary.

(1) The theory of the diffusion of colloidal electrolytes has been discussed. In order to obtain a value for the diffusion coefficient of such colloids as dyes it is necessary to use an equation which is an extension of the ordinary Nernst equation for the diffusion of electrolytes to the case of multivalent ions.

From this it is seen that we cannot obtain even qualitative results for the particle size from the diffusion coefficient. For example, if we have two dyes of the same high equivalent conductivity, but of different degrees of aggregation, we find that not only will the diffusion coefficients be high in each case, but the dye with the higher degree of aggregation may actually have the higher diffusion coefficient.

(2) If the diffusion of the colloidal dye takes place in the presence of other electrolytes, the potential gradient which arises during the diffusion of the pure dye is reduced and consequently we get a drop in the diffusion coefficient. As the concentration of the added electrolyte becomes large compared to that of the colloidal electrolyte, we approach a limiting case where the ions of the colloidal electrolyte diffuse independently. The relationship between the diffusion coefficient and the radius of the (colloidal) ion is then given by the Stokes-Einstein equation. It will therefore be possible to make use of this principle for obtaining a value for the radius of the particle in those cases where the degree of aggregation is not influenced by the concentration of electrolyte necessary to eliminate the potential gradient.

(3) The influence of electrolytes in thus reducing the diffusion coefficient of the dye accounts for the low diffusion coefficients that have often been reported, the electrolytes having been present as impurities. The effect, of course, will be further complicated in some cases by the electrolyte altering the degree of aggregation.

(4) It has also been shown that the influence of the electrical forces on the diffusion coefficient must be taken into account in the case of charged colloids not generally treated as colloidal electrolytes. In this way it is not only possible to account for the otherwise unexpectedly high results obtained by Bruins for the diffusion coefficients of starch and gum arabic, but also for the magnitude of the drop in the diffusion coefficient which he obtained on the addition of small quantities of electrolytes. The, at first sight, surprisingly large effect in these cases is due to the very high "equivalent weight" of the charged colloid.

In those cases of charged colloids where diffusion coefficients have been obtained in concordance with the Stokes-Einstein equation, there were probably sufficient electrolytes present as a result of the method of preparation of the sol to eliminate the effect due to a potential gradient.

Our thanks are due to Professor F. G. Donnan, C.B.E., F.R.S., for the interest he has taken in this research.

Arc Spectrum of Gold.

By Professor J. C. McLennan, F.R.S., and A. B. McLay.*

(Received September 11, 1931.)

Wave-lengths of the alkali-like doublet spectrum of gold, Au I, were identified by Thorsen† in 1923. The validity of Thorsen's analysis depended on the correctness of his choice of the resonance lines, $6s\,^2S—6p\,^2P^0$. The classification of these was confirmed and what was believed to be (but see below) the second member of the $^2S—^2P^0$ series identified by the authors‡ who, two years later, observed absorption of the two pairs of wave-lengths by normal vapour of gold. A metastable term of inverted ^2D type and a higher one with $^2P^0$ characteristics that did not belong to the simple doublet spectrum were evaluated by us also.

In a subsequent investigation§ of Au I, the authors found that the value of one component of the metastable ^2D term was not real and succeeded in re-evaluating the level correctly. A number of higher terms in addition to the irregular $^2P^0$ was observed also. These and the metastable ^2D term were shown to be a part of the complex spectrum built on the $5d\,6s$ ion and predicted by the Hund theory that had been just then introduced. L and S values were assigned tentatively by us to many of these terms; but changes in some of the values were suggested later by Symons and Daley|| after they had carried out a Zeeman effect analysis of gold arc lines.

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† 'Naturw.,' vol. 11, p. 500 (1923).

‡ 'Proc. Roy. Soc.,' A, vol. 108, p. 571 (1925).

§ 'Proc. Roy. Soc.,' A, vol. 112, p. 95 (1926).

|| 'Phys. Soc. Proc.,' vol. 41, p. 431 (1929).

The $5f\,^2F^0$ term of the one-electron spectrum and a few new terms of the many-electron spectrum of Au I have been identified recently by us. $5f\,^2F^0$ of Au I is inverted like the corresponding ones of Hg II* and Tl III†. From the disposition of all the known terms that originate in complex electronic configurations of the neutral gold atom, it is now evident that the couplings of electronic quantum vectors are more nearly of the *jj* than of the LS (Russell-Saunders) type. Little significance, therefore, can be attached to the LS assignments made earlier by the authors (*loc. cit.*), or by Symons and Daley (*loc. cit.*).

The present investigation has been carried out in conjunction with similar analyses of the analogous many-electron spectra of Hg II and Tl III. The results of the analyses of the latter two spectra will be published at an early date by the authors and M. F. Crawford. If the progression of values of similar terms in Au I, Hg II and Tl III could be traced, the classification of observed levels of each spectrum in terms of their electronic origins would be more certain than if made only with a knowledge of the disposition of levels in that spectrum. Only a few such progressions have been established satisfactorily as yet. The interpretations of Au I, Hg II and Tl III have been facilitated also by a knowledge of certain important levels of the spark spectra Au II,‡§ Hg III§|| and Tl IV,§ and of the progressions of values of corresponding levels in this sequence which have been identified and discussed by Mack.§

The terms of Au I and their values based on zero value for the deepest, 6*s* S, are recorded in Table I. The electronic configurations from which many of them most probably originate are indicated in the table with *j* values of the electrons added, wherever these are reasonably certain. Terms that are known definitely to belong to the single-electron spectrum are designated by Russell-Saunders' notation since their L, S and J values can be determined unambiguously. But because of the approach to *jj* coupling only J values of terms of many-electron configurations can be assigned uniquely, unless any of them are independent of coupling, in which case their L and S characteristics are unambiguous. In order, however, to have a uniform system of notation for the complex spectrum, all the terms that belong to it have been designated by Arabic numerals with J value subscripts. Some high ^2S and ^2D series

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* Paschen, 'Sitz. Preuss. Akad. Wiss.,' vol. 32, p. 536 (1928).

† McLennan, McLay and Crawford, 'Proc. Roy. Soc.,' A, vol. 125, p. 50 (1929).

‡ McLennan, McLay, 'Trans. Roy. Soc. Canada,' vol. 22, p. 103 (1928).

§ Mack, 'Phys. Rev.,' vol. 34, p. 17 (1929).

|| McLennan, McLay and Crawford, 'Trans. Roy. Soc. Canada,' vol. 22, p. 247 (1928).

members of the one-electron spectrum, observed by Thorsen (*loc. cit.*), have been omitted from Table I because they do not seem to us to be definitely established.

Table I.

Configuration.	Level.		Configuration.	Level.	
$6s_{\frac{1}{2}}$	$6s\,{}^2S_{\frac{1}{2}}$	0·0		$17^0{}_{2\frac{1}{2}}$	61255·4
$5d^9{}_{2\frac{1}{2}}\ 6s^2{}_0$	$1_{2\frac{1}{2}}$	9160·8		$18^0{}_{\frac{1}{2}}$	61563·0
$5d^9{}_{1\frac{1}{2}}\ 6s^2{}_0$	$2_{1\frac{1}{2}}$	21434·8	$6d_{1\frac{1}{2}}$	$6d\,{}^2D_{1\frac{1}{2}}$	61951·5
$6p_{\frac{1}{2}}$	$6p\,{}^2P^0{}_{\frac{1}{2}}$	37358·8	$6d_{2\frac{1}{2}}$	$6d\,{}^2D_{2\frac{1}{2}}$	62033·9
$6p_{1\frac{1}{2}}$	$6p\,{}^2P^0{}_{1\frac{1}{2}}$	41174·0		$19^0{}_{1\frac{1}{2}}$	63005·1
$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6p_{\frac{1}{2}}$	$1^0{}_{2\frac{1}{2}}$	42163·0		$20^0{}_{2\frac{1}{2}}$	63712·9
$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6p_{\frac{1}{2}}$	$2^0{}_{3\frac{1}{2}}$	45536·7	$8s_{\frac{1}{2}}$	$8s\,{}^2S_{\frac{1}{2}}$	64742·4
$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6p_{\frac{1}{2}}$	$3^0{}_{2\frac{1}{2}}$	46174·5	$5f_{3\frac{1}{2}}$	$5f\,{}^2F^0{}_{3\frac{1}{2}}$	67359·0
$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6p_{\frac{1}{2}}$	$4^0{}_{1\frac{1}{2}}$	47007·0	$5f_{2\frac{1}{2}}$	$5f\,{}^2F^0{}_{2\frac{1}{2}}$	67369·2
$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6p_{1\frac{1}{2}}$	$5^0{}_{4\frac{1}{2}}$	48696·5	$7d_{1\frac{1}{2}}$	$7d\,{}^2D_{1\frac{1}{2}}$	67469·1
$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6p_{1\frac{1}{2}}$	$6^0{}_{3\frac{1}{2}}$	51028·4	$7d_{2\frac{1}{2}}$	$7d\,{}^2D_{2\frac{1}{2}}$	67510·9
$5d^9{}_{1\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6p_{\frac{1}{2}}$	$7^0{}_{1\frac{1}{2}}$	51231·0	$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 7s_{\frac{1}{2}}$	$3_{3\frac{1}{2}}$	67810·8
$5d^9\ 6s\ 6p$	$8^0{}_{2\frac{1}{2}}$	51653·1	$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 7s_{\frac{1}{2}}$	$4_{2\frac{1}{2}}$	68704·6
$5d^9{}_{1\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6p_{\frac{1}{2}}$	$9^0{}_{\frac{1}{2}}$	53195·8	$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 7s_{\frac{1}{2}}$	$5_{1\frac{1}{2}}$	70652·7
$7s_{\frac{1}{2}}$	$7s\,{}^2S_{\frac{1}{2}}$	54484·8	$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6d$	$6_{1\frac{1}{2}}$	76257·3
$5d^9\ 6s\,6p$	$10^0{}_{1\frac{1}{2}}$ (or $_{2\frac{1}{2}}$)	56105·4	$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6d$	$7_{4\frac{1}{2}}$	76481·7
$5d^9\ 6s\,6p$	$11^0{}_{2\frac{1}{2}}$	58616·2	$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6d$	$8_{2\frac{1}{2}}$	76565·7
	$12^0{}_{3\frac{1}{2}}$	58845·3	$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6d_{2\frac{1}{2}}$	$9_{5\frac{1}{2}}$	76569·3
	$13^0{}_{3\frac{1}{2}}$	59363·1	$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6d$	$10_{3\frac{1}{2}}$	76731·5
	$14^0{}_{3\frac{1}{2}}$	59713·3	$5d^9{}_{2\frac{1}{2}}\ 6s_{\frac{1}{2}}\ 6d$	$11_{4\frac{1}{2}}$	76829·2
	$15^0{}_{\frac{1}{2}}$	60032·5			
	$16^0{}_{1\frac{1}{2}}$	60728·2	$5d^{10}{}_0$ of Au^+	${}^1S_0$	~74461·0

Classified wave-lengths of Au I are given in Table II. The wave-length and intensity values were obtained from a number of sources, which are indicated by the symbols in the right-hand column and at the heads of the intensity lists respectively, with references to these symbols at the end of the table. A number of the wave-lengths classified in Au I are listed only as spark lines in Kayser and Konen's 'Handbuch,' vol. 7. But most of these have been identified by us on plates of both the arc and spark spectra of gold obtained during our previous investigations of Au I and Au II. A comparison of relative intensities of these lines in the two types of source showed that they belong undoubtedly to Au I. The correspondence of observed wave-numbers and those calculated from term differences is fairly good except for ones in the infra-red region where the accuracy of measurement is not high. However, the validity of the term scheme of Table I would not be impaired even if some of the infra-red lines were found to be incorrectly classified.

All wave-lengths that have been classified as $6s\,{}^2S_{\frac{1}{2}}$ combinations in Table II were observed by us to be absorbed by normal gold vapour in our previous investigations (*loc. cit.*), except the two ultra-violet lines λ 1624 A, $6s\,{}^2S_{\frac{1}{2}}$—$18^0{}_{\frac{1}{2}}$,

Table II.

Intensity.				λ (I.A.).	ν.	Classification.	Observer.
M_1	V(*a*)						
15	5			7510·74	13310·6	$6p\ {}^2\mathrm{P}^0_{1\frac{1}{2}}$ — $7s\ {}^2\mathrm{S}_{\frac{1}{2}}$	V(*a*)
1				7281·8	13729	$20^0_{2\frac{1}{2}}$ — $10_{3\frac{1}{2}}$	M_1
3				6873·5	14544	$10^0_{1\frac{1}{2}}$ — $5_{1\frac{1}{2}}$	,,
		Q					
7		—		6652·6	15028	$4^0_{1\frac{1}{2}}$ — $6d\ {}^2\mathrm{D}_{2\frac{1}{2}}$	,,
2		—		6530·2	15309	$17^0_{2\frac{1}{2}}$ — $8_{2\frac{1}{2}}$	,,
5		—		6436·2	15533	$16^0_{1\frac{1}{2}}$ — $6_{1\frac{1}{2}}$	,,
1		—		6337·4	15775	$3^0_{2\frac{1}{2}}$ — $6d\ {}^2\mathrm{D}_{1\frac{1}{2}}$	,,
4		—		12·8	15837	$16^0_{1\frac{1}{2}}$ — $8_{2\frac{1}{2}}$	,,
2		—		02·2	15863	$3^0_{2\frac{1}{2}}$ — $6d\ {}^2\mathrm{D}_{2\frac{1}{2}}$	,,
	H(*a*)		M_2				
15	4	4	12	6278·18	15923·8	$2_{1\frac{1}{2}}$ — $6p\ {}^2\mathrm{P}^0_{\frac{1}{2}}$	Q
3	—	—	—	6160·1	16229	$15^0_{\frac{1}{2}}$ — $6_{1\frac{1}{2}}$	M_1
10	1	1*u*	5	5956·98	16782·4	$6^0_{3\frac{1}{2}}$ — $3_{3\frac{1}{2}}$	Q
2	—	—	—	33·7	16848	$14^0_{3\frac{1}{2}}$ — $8_{2\frac{1}{2}}$	M_1
10	1*u*	1*u*	4	5862·94	17051·6	$8^0_{2\frac{1}{2}}$ — $4_{2\frac{1}{2}}$	Q
15	3	4	10	37·40	17126·5′	$6p\ {}^2\mathrm{P}^0_{\frac{1}{2}}$ — $7s\ {}^2\mathrm{S}_{\frac{1}{2}}$	,,
—	—	—	1	5726·82	17456·9	$9^0_{\frac{1}{2}}$ — $5_{1\frac{1}{2}}$	V(*s*)
—	—	—	1	21·26	17473·8	$7^0_{1\frac{1}{2}}$ — $4_{2\frac{1}{2}}$	M_2
10	1	1	5	5655·76	17676·2	$6^0_{3\frac{1}{2}}$ — $4_{2\frac{1}{2}}$	Q
	—	—	2	5261·82	18999·6	$8^0_{2\frac{1}{2}}$ — $5_{1\frac{1}{2}}$	V(*s*)
	2	1*u*	8	30·31	19114·0	$5^0_{4\frac{1}{2}}$ — $3_{3\frac{1}{2}}$	Q
	—	—	2	5147·39	19421·9	$7^0_{1\frac{1}{2}}$ — $5_{1\frac{1}{2}}$	M_2
	2	2*u*	7	5064·62	19739·4	$2_{1\frac{1}{2}}$ — $6p\ {}^2\mathrm{P}^0_{1\frac{1}{2}}$	Q
	3	4*u*	8	4811·61	20777·3	$6p\ {}^2\mathrm{P}^0_{1\frac{1}{2}}$ — $6d\ {}^2\mathrm{D}_{1\frac{1}{2}}$	,,
	10	8	18	4792·60	20859·7	$6p\ {}^2\mathrm{P}^0_{1\frac{1}{2}}$ — $6d\ {}^2\mathrm{D}_{2\frac{1}{2}}$	,,
	—	—	1	4620·70	21635·7	$3^0_{2\frac{1}{2}}$ — $3_{3\frac{1}{2}}$	M_2
	1?	4	6	07·35	21698·4	$4^0_{1\frac{1}{2}}$ — $4_{2\frac{1}{2}}$	Q
	2	4	10	4488·26	22274·1	$2^0_{3\frac{1}{2}}$ — $3_{3\frac{1}{2}}$	,,
	4	4	6	4437·28	22530·0	$3^0_{2\frac{1}{2}}$ — $4_{2\frac{1}{2}}$	,,
	2	1	9	4315·11	23167·9	$2^0_{3\frac{1}{2}}$ — $4_{2\frac{1}{2}}$	,,
	1	2*u*	5	4241·84	23568·2	$6p\ {}^2\mathrm{P}^0_{1\frac{1}{2}}$ — $8s\ {}^2\mathrm{S}_{\frac{1}{2}}$	,,
	—	1*u*	5	4084·14	24478·1	$3^0_{2\frac{1}{2}}$ — $5_{1\frac{1}{2}}$	,,
	3	6	15	65·08	24592·8	$6p\ {}^2\mathrm{P}^0_{\frac{1}{2}}$ — $6d\ {}^2\mathrm{D}_{1\frac{1}{2}}$	,,
	1	2	10	40·95	24739·7	$2_{1\frac{1}{2}}$ — $3^0_{2\frac{1}{2}}$	,,
	—	6R?	2	3927·6	25454	$6^0_{3\frac{1}{2}}$ — $7_{4\frac{1}{2}}$	H(*s*)
	—	—	2	14·7	25538	$6^0_{3\frac{1}{2}}$ — $8_{2\frac{1}{2}}$	,,
	1	2	7	09·39	25572·2	$2_{1\frac{1}{2}}$ — $4^0_{1\frac{1}{2}}$	Q
	—	4	15	3897·88	25647·7	$1^0_{2\frac{1}{2}}$ — $3_{3\frac{1}{2}}$	,,
	—	—	2	89·45	25703·3	$6^0_{3\frac{1}{2}}$ — $10_{3\frac{1}{2}}$	H(*s*)
	—	1	3	75·08	25800·8	$6^0_{3\frac{1}{2}}$ — $11_{4\frac{1}{2}}$	Q
	—	—	2	01·97	26294·7	$6p\ {}^2\mathrm{P}^0_{1\frac{1}{2}}$ — $7d\ {}^2\mathrm{D}_{1\frac{1}{2}}$	M_2
	—	—	10	3795·90	26336·7	$6p\ {}^2\mathrm{P}^0_{1\frac{1}{2}}$ — $7d\ {}^2\mathrm{D}_{2\frac{1}{2}}$	H(*s*)
	—	—	4	3650·75	27383·8	$6p\ {}^2\mathrm{P}^0_{\frac{1}{2}}$ — $8s\ {}^2\mathrm{S}_{\frac{1}{2}}$	,,
	—	—	2	3598·08	27784·7	$5^0_{4\frac{1}{2}}$ — $7_{4\frac{1}{2}}$	,,
	—	—	12	86·70	27872·8	$5^0_{4\frac{1}{2}}$ — $9_{5\frac{1}{2}}$	,,
	—	—	2	65·9	28035	$5^0_{4\frac{1}{2}}$ — $10_{3\frac{1}{2}}$	,,
	—	—	5	53·56	28132·8	$5^0_{4\frac{1}{2}}$ — $11_{4\frac{1}{2}}$	,,
	—	—	2	3382·0	29560	$4^0_{1\frac{1}{2}}$ — $8_{2\frac{1}{2}}$	,,
	—	—	4	55·18	29796·1	$2_{1\frac{1}{2}}$ — $7^0_{1\frac{1}{2}}$	,,
	—	—	—	23·2?	30083	$3^0_{2\frac{1}{2}}$ — $6_{1\frac{1}{2}}$	,,
	1	2	8	20·14	30110·2	$6p\ {}^2\mathrm{P}^0_{\frac{1}{2}}$ — $7d\ {}^2\mathrm{D}_{1\frac{1}{2}}$	Q
	1	2	10	08·31	30218·3	$2_{1\frac{1}{2}}$ — $8^0_{2\frac{1}{2}}$	,,
	—	1*u*	9	3230·61	30945·0	$2^0_{3\frac{1}{2}}$ — $7_{4\frac{1}{2}}$	,,
	—	4*u*	7	04·74	31194·7	$2^0_{3\frac{1}{2}}$ — $10_{3\frac{1}{2}}$	,,
	—	4*u*	5	3194·73	31292·5	$2^0_{3\frac{1}{2}}$ — $11_{4\frac{1}{2}}$	,,
	—	—	2	47·6	31761	$2_{1\frac{1}{2}}$ — $9^0_{\frac{1}{2}}$	M_2

Table II—(continued).

Intensity.			λ (I.A.).	ν.	Classification.	Observer.
H(*a*)	Q	M_2				
10	8	15	3122·78	32013·5	$1_{2\frac{1}{2}}$ — $6p\ {}^2P^0_{1\frac{1}{2}}$	Q
8	8*v*	15	3029·22	33002·2	$1_{2\frac{1}{2}}$ — $1^0_{2\frac{1}{2}}$	,,
1	5	6	2932·19	34094·3	$1^0_{2\frac{1}{2}}$ — $6_{1\frac{1}{2}}$	,,
1	6	5	05·90	34402·7	$1^0_{2\frac{1}{2}}$ — $8_{2\frac{1}{2}}$	,,
—	4	4	2891·96	34568·5	$1^0_{2\frac{1}{2}}$ — $10_{3\frac{1}{2}}$	,,
1	5	8	83·46	34670·4	$2_{1\frac{1}{2}}$ — $10^0_{1\frac{1}{2}}$	,,
4	6	15	2748·26	36375·9	$1_{2\frac{1}{2}}$ — $2^0_{3\frac{1}{2}}$	,,
2	4	12	00·90	37013·7	$1_{2\frac{1}{2}}$ — $3^0_{2\frac{1}{2}}$	,,
1	4	10	2688·72	37181·4	$2_{1\frac{1}{2}}$ — $11^0_{2\frac{1}{2}}$	,,
15	10R	20R	75·95	37358·8	$6s\ {}^2S_{\frac{1}{2}}$ — $6p\ {}^2P^0_{\frac{1}{2}}$	,,
2	4	12	41·49	37846·1	$1_{2\frac{1}{2}}$ — $4^0_{1\frac{1}{2}}$	,,
1	4	8	2590·05	38597·7	$2_{1\frac{1}{2}}$ — $15^0_{\frac{1}{2}}$	,,
—	4	6	44·20	39293·4	$2_{1\frac{1}{2}}$ — $16^0_{1\frac{1}{2}}$	,,
—	4	8	10·50	39820·6	$2_{1\frac{1}{2}}$ — $17^0_{2\frac{1}{2}}$	,,
—	—	4	2491·25	40128·2	$2_{1\frac{1}{2}}$ — $18^0_{\frac{1}{2}}$	M_2
5R	10R	25R	27·98	41174·0	$6s\ {}^2S_{\frac{1}{2}}$ — $6p\ {}^2P^0_{1\frac{1}{2}}$	Q
—	—	4	04·83	41570·3	$2_{1\frac{1}{2}}$ — $19^0_{1\frac{1}{2}}$	H(*s*)
1	5	10	2387·75	41867·6	$1_{2\frac{1}{2}}$ — $6^0_{3\frac{1}{2}}$	Q
—	4	6	76·25	42070·3	$1_{2\frac{1}{2}}$ — $7^0_{1\frac{1}{2}}$	,,
—	4	5	64·57	42278·1	$2_{1\frac{1}{2}}$ — $20^0_{2\frac{1}{2}}$	,,
1	6	8	52·65	42492·2	$1_{2\frac{1}{2}}$ — $8^0_{2\frac{1}{2}}$	,,
		2	2176·33	45934·4	$2_{1\frac{1}{2}}$ — $5f\ {}^2F^0_{2\frac{1}{2}}$	M_2
		3	29·46	46945·4	$1_{2\frac{1}{2}}$ — $10^0_{1\frac{1}{2}}$	,,
		4	26·66	47007·2	$6s\ {}^2S_{\frac{1}{2}}$ — $4^0_{1\frac{1}{2}}$	,,
	S					
	7	6	2021·38	49455·3	$1_{2\frac{1}{2}}$ — $11^0_{2\frac{1}{2}}$	S
	12*n*	10	12·05	49684·5	$1_{2\frac{1}{2}}$ — $12^0_{3\frac{1}{2}}$	,,
			λ (I vac.).			
	10	6	1991·94	50202·3	$1_{2\frac{1}{2}}$ — $13^0_{3\frac{1}{2}}$	,,
	15	12	1978·14	50552·5	$1_{2\frac{1}{2}}$ — $14^0_{3\frac{1}{2}}$	,,
	7	6	51·97	51230·3	$6s\ {}^2S_{\frac{1}{2}}$ — $7^0_{1\frac{1}{2}}$	,,
	5	5	39·24	51566·6	$1_{2\frac{1}{2}}$ — $16^0_{1\frac{1}{2}}$	,,
	8	8	19·63	52093·4	$1_{2\frac{1}{2}}$ — $17^0_{2\frac{1}{2}}$	,,
	6	6	1879·87	53195·2	$6s\ {}^2S_{\frac{1}{2}}$ — $9^0_{\frac{1}{2}}$	,,
	4	4	57·22	53843·9	$1_{2\frac{1}{2}}$ — $19^0_{1\frac{1}{2}}$	,,
	5		33·14	54551·2	$1_{2\frac{1}{2}}$ — $20^0_{2\frac{1}{2}}$	,,
	2		1718·27	58198·1	$1_{2\frac{1}{2}}$ — $5f\ {}^2F^0_{3\frac{1}{2}}$	,,
	1		1665·73	60033·7	$6s\ {}^2S_{\frac{1}{2}}$ — $15^0_{\frac{1}{2}}$	,,
	0		46·66	60729·0	$6s\ {}^2S_{\frac{1}{2}}$ — $16^0_{1\frac{1}{2}}$	,,
			24·34	61563	$6s\ {}^2S_{\frac{1}{2}}$ — $18^0_{\frac{1}{2}}$	M_2
			1587·11	63008	$6s\ {}^2S_{\frac{1}{2}}$ — $19^0_{1\frac{1}{2}}$	,,

M_1 McLennan, Smith and Peters, 'Trans. Roy. Soc. Can.,' vol. 19, III, p. 39 (1925).
M_2 McLennan and McLay, 'Proc. Roy. Soc.,' A, vol. 112, p. 95 (1926), or this investigation.
V Eder and Valenta, Kayser and Konen, 'Handbuch der Spectroscopie,' vol. 7 (*a*) arc, (*s*) spark.
H Exner and Haschek, Kayser and Konen, 'Handbuch der Spectroscopie,' vol. 7; (*a*) arc, (*s*) spark.
Q Quincke, Kayser and Konen, 'Handbuch der Spectroscopie,' vol. 7.
S Selwyn, 'Phys. Soc. Proc.,' vol. 41, p. 392 (1929).

and λ 1587 A, $6s\,^2S_{\frac{1}{2}}$—$19^0_{1\frac{1}{2}}$. These last two were found by us more recently to be absorbed definitely on careful re-inspection of our original absorption plates, after identification of the terms $18^0_{\frac{1}{2}}$ and $19^0_{1\frac{1}{2}}$. All wave-lengths classified as $6s\,^2S_{\frac{1}{2}}$ or $1_{2\frac{1}{2}}$ combinations were found previously to be reversed in the spectrum of an under-water spark between gold terminals (*loc. cit.*), except the ones below λ 1879 A. where the water becomes opaque. Three wave-lengths at λ 2111 A., λ 2082 A., and λ 2000 A. that were absorbed by the vapour of the spark under water were believed previously to be Au I lines but were classified later by us (*loc. cit.*) as combinations that involve low levels of Au II.

It should be pointed out that the terms designated $15^0_{\frac{1}{2}}$ and $16^0_{1\frac{1}{2}}$ in Table I were originally classified (*loc. cit.*) as components of $7p\,^2P^0$ of the doublet spectrum. We cannot be so certain of this now. The terms $18^0_{\frac{1}{2}}$ and $19^0_{1\frac{1}{2}}$ found since then might equally as well be the ones and in some respects fit into the one-electron spectrum better than the lower pair. Inasmuch as the $7p\,^2P^0$ term certainly lies within the region of and closely adjacent to odd terms of other configurations with similar J values, it is probable that it does not have unique characteristics. At any rate we have no certain means at present of distinguishing between the two possibilities mentioned above.

The term 1^0 was originally reported by us to have $J = 3\frac{1}{2}$ because it did not combine with $2_{1\frac{1}{2}}$. The lower value of J, $2\frac{1}{2}$, assigned to it in Table I, must be the correct one since the term undoubtedly belongs, together with $2^0_{3\frac{1}{2}}$, $3^0_{2\frac{1}{2}}$ and $4^0_{1\frac{1}{2}}$, to the isolated group $5d\ 9_{2\frac{1}{2}}\,[\leftarrow 6s_{\frac{1}{2}}\,[\leftarrow 6p_{\frac{1}{2}}$. Furthermore, this change was suggested earlier by Symons and Daley (*loc. cit.*) to account for the general type of Zeeman pattern of the combination of 1^0 with $1_{2\frac{1}{2}}$. The failure to observe the line $2_{1\frac{1}{2}}$—$1^0_{2\frac{1}{2}}$ is apparently due to an intensity anomaly characteristic of this type of spectrum with intermediate or near *jj* coupling, for the corresponding transition has not been observed by Shenstone* in Cu I or by the authors in Hg II or Tl III. The change in J of 1^0 has necessitated changing that of the term 10 from $4\frac{1}{2}$, as previously quoted by us, to $3\frac{1}{2}$ to account for an observed combination 1^0—10 (Table II). The value $1\frac{1}{2}$ for J of the odd term 10^0 is probably the correct one according to the Zeeman effect analysis of Au I by Symons and Daley (*loc. cit.*). Our results do not allow us to distinguish between this value and $2\frac{1}{2}$ since no combination line $6s\,^2S_{\frac{1}{2}}$—10^0 has been observed in emission or absorption.

The determination of the configurations to which some of the higher odd terms of Table I are to be attributed is somewhat complicated by the fact that

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* 'Phys. Rev.,' vol. 28, p. 449 (1926).

$7p$ terms and high $5d^9 [\leftarrow 6s\,6p$ ones intermix, as already pointed out; and also that low ones of $5d^8\,6s^2\,6p$ and of $5d^9\,6s\,7p$ are expected to have energy values in about the same region. A complete disentanglement of the origins of these observed levels may well be impossible therefore, but some further progress may be made in this direction after the investigation of the Au I iso-electronic sequence has been carried out more fully. A careful study of vector couplings of electrons in the atoms Au, Hg^+ and Tl^{++} is now being made and is being related to the couplings in the next ions Au^+, Hg^{++} and Tl^{+++}. Any important conclusions about couplings that may be made by this study will be reported in the forthcoming communication on Tl III.

Spark Spectrum of Mercury, Hg II.

By Professor J. C. McLennan, F.R.S., A. B. McLay,[*] and M. F. Crawford.

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The one-electron doublet spectrum of Hg II was analysed very thoroughly by Paschen[†] after a few of its most stable terms had been identified by Carroll.[‡] Minor features were added to the knowledge of its structure by Rasmussen[§] and by Naudé.[||] Paschen also identified the low inverted ^2D term and seven higher terms and Naudé a number of additional ones of the complex structure of Hg II that originates in many-electron configurations of the Hg^+ ion. Naudé assigned L and S characteristics to most of his and Paschen's complex terms.

The authors have recently been carrying out an investigation of the structures, that originate in complex configurations, of the iso-electronic Au I, Hg II and Tl III spectra. The analysis of Au I made some time ago by two of us[¶] has been extended and the interpretation of its complex structure modified somewhat in view of the fact that the couplings of quantum vectors of electrons of the neutral gold atom were found to be more nearly of the *jj* type than had been supposed previously. A similar conclusion about electron couplings in Hg^+ and Tl^{++} ions has been reached by us in our investigations of Hg II and Tl III spectra. A paper* on the structure of Au I has just been sent to press. The analysis of Tl III is not yet completed, but it is hoped that results can be published at an early date.

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[†] 'Sitz. Preuss. Akad. Wiss.,' vol. 32, p. 536 (1928).

[‡] 'Phil. Trans.,' A, vol. 225, p. 357 (1925).

[§] 'Naturw.,' vol. 17, p. 389 (1929).

[||] 'Ann. Physik,' vol. 5, p. 1 (1929).

[¶] 'Proc. Roy. Soc.,' A, vol. 112, p. 95 (1926).

In the case of the complex structure of Hg II we found, on reviewing the previous work of Paschen and Naudé that two of Paschen's (*loc. cit.*) and several of Naudé's (*loc. cit.*) terms were not well established. By re-investigating it we have identified some levels not observed by them. Our wave-number analysis, given in the following, differs considerably therefore from that of Naudé, which included his own and Paschen's energy levels; and because of the altered distribution of observed energy states, which indicates near *jj* coupling as noted above, our interpretation of the spectrum has little resemblance to that given by Naudé.

Table I.

Configuration.	Level.		Previous designation.†
$6s_{\frac{1}{2}}$	$6s\,{}^2S_{\frac{1}{2}}$	0	1S
$5d^9_{2\frac{1}{2}}\,6s^2_0$	$1_{2\frac{1}{2}}$	35514	*D_3
$5d^9_{1\frac{1}{2}}\,6s^2_0$	$2_{1\frac{1}{2}}$	50554	*D_2
$6p_{\frac{1}{2}}$	$6p\,{}^2P^0_{\frac{1}{2}}$	51485	$2P_1$
$6p_{1\frac{1}{2}}$	$6p\,{}^2P_{10\frac{1}{2}}$	60608	$2P_2$
$5d^9_{2\frac{1}{2}}\,6s_{\frac{1}{2}}\,6p_{\frac{1}{2}}$	$1^0_{2\frac{1}{2}}$	79704	
$5d^9_{2\frac{1}{2}}\,6s_{\frac{1}{2}}\,6p_{\frac{1}{2}}$	$2^0_{3\frac{1}{2}}$	84209	${}^4\bar{D}_{7/2}$
$5d^9_{2\frac{1}{2}}\,6s_{\frac{1}{2}}\,6p_{\frac{1}{2}}$	$3^0_{2\frac{1}{2}}$	84834	${}^4F_{5/2}$
$5d^9_{2\frac{1}{2}}\,6s_{\frac{1}{2}}\,6p_{\frac{1}{2}}$	$4^0_{1\frac{1}{2}}$	86177	${}^4P_{3/2}$
$5d^9_{2\frac{1}{2}}\,6s_{\frac{1}{2}}\,6p_{1\frac{1}{2}}$	$5^0_{4\frac{1}{2}}$	92566 ?	
$5d^9_{1\frac{1}{2}}\,6s_{\frac{1}{2}}\,6p_{\frac{1}{2}}$	$6^0_{1\frac{1}{2}}$	94091	${}^4F_{3/2}$
$5d^9_{2\frac{1}{2}}\,6s_{\frac{1}{2}}\,6p_{1\frac{1}{2}}$	$7^0_{3\frac{1}{2}}$	95186	
$5d^9\,6s\,6p$	$8^0_{2\frac{1}{2}}$	95302	
$7s_{\frac{1}{2}}$	$7s\,{}^2S_{\frac{1}{2}}$	95714	2S
$5d^9_{1\frac{1}{2}}\,6s_{\frac{1}{2}}\,6p_{\frac{1}{2}}$	$9^0_{\frac{1}{2}}$	96185	
$5d^9\,6s\,6p$	$10^0_{2\frac{1}{2}}$	97094	${}^4\bar{D}_{5/2}$
$5d^9\,6s\,6p$	$11^0(_{1\frac{1}{2}}\text{ or }_{2\frac{1}{2}})$	100859	${}^2F_{5/2}$
$5d^9\,6s\,6p$	$12^0_{1\frac{1}{2}}$	103183	${}^4\bar{D}_{3/2}$
$5d^9\,6s\,6p$	$13^0_{\frac{1}{2}}$	103872	$Z(P_1)$
$5d^9\,6s\,6p$	$14^0(_{1\frac{1}{2}}\text{ or }_{2\frac{1}{2}})$	104036	
$6d_{1\frac{1}{2}}$	$6d\,{}^2D_{1\frac{1}{2}}$	104983	$3D_2$
$6d_{2\frac{1}{2}}$	$6d\,{}^2D_{2\frac{1}{2}}$	105543	$3D_3$
$5d^9\,6s\,6p$	$15^0_{1\frac{1}{2}}$	106085	$Y(P_2)$
$5d^9_{2\frac{1}{2}}\,6s_{\frac{1}{2}}\,6p_{1\frac{1}{2}}$	$16^0_{3\frac{1}{2}}$	106213	
	$17^0_{\frac{1}{2}}$	106295	$U(P_1)$
	$18^0_{1\frac{1}{2}}$	106714	${}^2F_{7/2}$
	$19^0_{\frac{1}{2}}$	108298	$3P_1$
	$20^0_{3\frac{1}{2}}$	108974	
	$21^0_{1\frac{1}{2}}$	109189	$X(P_2)$
	$22^0_{1\frac{1}{2}}$	110603	
	$23^0_{3\frac{1}{2}}$	111172	
	$24^0_{1\frac{1}{2}}$	111970	$3P_2$
$8s_{\frac{1}{2}}$	$8s\,{}^2S_{\frac{1}{2}}$	121416	3S
	$25^0_{2\frac{1}{2}}$	121959	$C(F_3)$
$5f_{3\frac{1}{2}}$	$5f\,{}^2F^0_{3\frac{1}{2}}$	123152	$4F_4$
$5f_{2\frac{1}{2}}$	$5f\,{}^2F^0_{2\frac{1}{2}}$	123409	$4F_3$
$7d_{1\frac{1}{2}}$	$7d\,{}^2D_{1\frac{1}{2}}$	125324	$4D_2$
$7d_{2\frac{1}{2}}$	$7d\,{}^2D_{2\frac{1}{2}}$	125578	$4D_3$
$9s_{\frac{1}{2}}$	$9s\,{}^2S_{\frac{1}{2}}$	132559	4S
$5g$	$5g\,{}^2G$	133653	5G
$8d_{1\frac{1}{2}}$	$8d\,{}^2D_{1\frac{1}{2}}$	134562	$5D_2$
$8d_{2\frac{1}{2}}$	$8d\,{}^2D_{2\frac{1}{2}}$	134698	$5D_3$
$5d^9_{2\frac{1}{2}}\,6s_{\frac{1}{2}}\,7s_{\frac{1}{2}}$?	$3_{3\frac{1}{2}}$	135299	
$5d^9_{2\frac{1}{2}}\,6s_{\frac{1}{2}}\,7s_{\frac{1}{2}}$?	$4_{2\frac{1}{2}}$	136712	${}^4D^3_{5/2}$
$5d^9_{2\frac{1}{2}}\,6s_{\frac{1}{2}}\,7s_{\frac{1}{2}}$?	$5_{2\frac{1}{2}}$	140135	${}^4D^3_{3/2}$
$5d_0^{10}$ of Hg^{++}	${}^1S_0$	~151280	

† Paschen, Term Table, *loc. cit.*; Naudé, Table VII, *loc. cit.*; Rasmussen, evaluation of $5g\,{}^2G$, *loc. cit.*

Table I is a list of all known levels of the many-electron spectrum of Hg II and, in addition, some of the more stable simple doublet terms of Paschen

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* 'Proc. Roy. Soc.,' A, vol. 134, p. 35 (1931).

(*loc. cit.*) that combine with them. Term values are based on the value zero for the deepest, $6s$ S, of the whole Hg II spectrum. The term notation is the same as that used by us in our latest communication (*loc. cit.*) on Au I. The designations of Paschen and of Naudé are given for purposes of comparison. Any many-electron terms reported by them that are not included in Table I are believed by us to be not sufficiently well established. It will be seen from Table I that the terms $19^0_{\frac{1}{2}}$ and $24^0_{1\frac{1}{2}}$ were interpreted by Paschen as 3P ($7p\ ^2P^0$ in our notation) components. But, just as in Au I (*loc. cit.*), the $7p\ ^2P^0$ term and $5d^9\,6s\,6p$ terms with similar J values probably lie close together, and therefore differentiation of characteristics is difficult if not actually meaningless.

The configurations, with j values of electrons added in some cases, assigned by us to certain terms of the complex structure are those that can be determined with any certainty at present. They were arrived at by a consideration of the distribution of levels of Hg II in groups; and by comparison of this with the distribution of levels of Au I (*loc. cit.*) and of Tl III. A knowledge of important states of the next spark spectrum of mercury, Hg III,* was also useful. Some of the odd levels of the complex structure have not been attributed to configurations because $7p$ terms and high $5d^9\,6s\,6p$ ones intermix and also low terms of $5d^8\,6s^2\,6p$ are expected in about the same region. The existence of five odd terms, each with $J = 3\frac{1}{2}$, if the J values are correct, is enough to indicate that at least one of them must arise from the last configuration, since only four of them are expected from $5d^9\,6s\,6p$ and none from $7p$. The disentanglement of origins of terms in the region of the overlapping groups will be extremely difficult.

Table II is a classified list of those wave-lengths of Hg II that involve many-electron terms, either in combination with one another or a combination of one of them with an ordinary doublet term. The wave-length and intensity values were obtained from a number of sources, which are indicated by the symbols in the right-hand column and at the heads of intensity lists, with references to these symbols at the end of the table. It should be pointed out that Naudé's list (*loc. cit.*) of lines of the mercury spectrum does not include any that were classified as Hg II lines by Paschen (*loc. cit.*); but he observed many more wave-lengths in the spectrum of a discharge in a hollow-cathode tube source containing pure mercury vapour than he or Paschen observed in that of a tube of the same type with a helium-mercury vapour mixture. The few wave-

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* McLennan, McLay and Crawford, 'Trans. Roy. Soc. Canada,' vol. 22, p. 247 (1928); Mack, 'Phys. Rev.,' vol. 34, p. 17 (1929).

Table II.

Intensity.			λ (I.A.).	ν.	Classification.	Observer.	Remarks.
R							
3			10590	9441	$24^{0}_{1\frac{1}{2}}$ — $8s\ {}^{2}S_{\frac{1}{2}}$	R	
4			9946·0	10051	$2_{1\frac{1}{2}}$ — $6p\ {}^{2}P^{0}_{1\frac{1}{2}}$	,,	
6			9639·0	10372	$7s\ {}^{2}S_{\frac{1}{2}}$ — $15^{0}_{1\frac{1}{2}}$	,,	
10			8548·2	11695	$25^{0}_{2\frac{1}{2}}$ — $5g\ {}^{2}G$	,,	
5*d*		P	8406·2	11892	$5f\ {}^{2}F^{0}_{2\frac{1}{2}}$ — $3_{3\frac{1}{2}}$	,,	
6		—	8177·6	12225	$21^{0}_{1\frac{1}{2}}$ — $8s\ {}^{2}S_{\frac{1}{2}}$	,,	
20		8	7944·66	12583·7	$7s\ {}^{2}S_{\frac{1}{2}}$ — $19^{0}_{\frac{1}{2}}$	P	
10		0	7621·3	13118	$19^{0}_{\frac{1}{2}}$ — $8s\ {}^{2}S_{\frac{1}{2}}$	,,	
	N						
—	1	—	7515·9	13301	$5f\ {}^{2}F^{0}_{2\frac{1}{2}}$ — $4_{2\frac{1}{2}}$	N	
10	*	0	7485·87	13354·6	$24^{0}_{1\frac{1}{2}}$ — $7d\ {}^{2}D_{1\frac{1}{2}}$	P	
8	*	6	18·1	13477	$7s\ {}^{2}S_{\frac{1}{2}}$ — $21^{0}_{1\frac{1}{2}}$	,,	
20	*	4	7346·37	13608·4	$24^{0}_{1\frac{1}{2}}$ — $7d\ {}^{2}D_{2\frac{1}{2}}$	,,	
4	*	0?	6938·1	14409	$23^{0}_{3\frac{1}{2}}$ — $7d\ {}^{2}D_{2\frac{1}{2}}$	R	*a*
4	—	—	6715·2	14887	$7s\ {}^{2}S_{\frac{1}{2}}$ — $22^{0}_{1\frac{1}{2}}$	,,	
1*d*	—	—	6675·5	14976	$22^{0}_{1\frac{1}{2}}$ — $7d\ {}^{2}D_{2\frac{1}{2}}$	,,	
1	2	—	46·7	15041	$1_{2\frac{1}{2}}$ — $2_{1\frac{1}{2}}$?	N	*b*
—	*	1	09·8	15124	$17^{0}_{\frac{1}{2}}$ — $8s\ {}^{2}S_{\frac{1}{2}}$	P	
8	*	2	6521·13	15330·5	$15^{0}_{1\frac{1}{2}}$ — $8s\ {}^{2}S_{\frac{1}{2}}$	,,	
3	—	—	6196·3	16134	$21^{0}_{1\frac{1}{2}}$ — $7d\ {}^{2}D_{1\frac{1}{2}}$	R	
20	*	20	49·50	16257·0	$7s\ {}^{2}S_{\frac{1}{2}}$ — $24^{0}_{1\frac{1}{2}}$	P	
5	*	0	00·0	16389	$21^{0}_{1\frac{1}{2}}$ — $7d\ {}^{2}D_{2\frac{1}{2}}$	,,	
5	—	—	6089·8	16416	$6d\ {}^{2}D_{2\frac{1}{2}}$ — $25^{0}_{2\frac{1}{2}}$	R	
	*	4	5888·94	16976·3	$6d\ {}^{2}D_{1\frac{1}{2}}$ — $25^{0}_{2\frac{1}{2}}$	P	
	*	6	71·73	17026·0	$19^{0}_{\frac{1}{2}}$ — $7d\ {}^{2}D_{1\frac{1}{2}}$	,,	
	*	3	5698·69	17543·0	$13^{0}_{\frac{1}{2}}$ — $8s\ {}^{2}S_{\frac{1}{2}}$	,,	
	1	—	5499·8	18177	$25^{0}_{2\frac{1}{2}}$ — $5_{2\frac{1}{2}}$	N	
	2	—	5371·42	18611·9	$18^{0}_{1\frac{1}{2}}$ — $7d\ {}^{2}D_{1\frac{1}{2}}$	,,	
	2	—	5299·53	18864·5	$18^{0}_{1\frac{1}{2}}$ — $7d\ {}^{2}D_{2\frac{1}{2}}$	,,	
	*	4	5196·15	19239·6	$15^{0}_{1\frac{1}{2}}$ — $7d\ {}^{2}D_{1\frac{1}{2}}$	P	
	1	—	5162·15	19366·4	$4^{0}_{1\frac{1}{2}}$ — $6d\ {}^{2}D_{2\frac{1}{2}}$ $16^{0}_{3\frac{1}{2}}$ — $7d\ {}^{2}D_{2\frac{1}{2}}$	N	
	*	10	28·45	19493·6	$15^{0}_{1\frac{1}{2}}$ — $7d\ {}^{2}D_{2\frac{1}{2}}$	P	
	3	—	4961·89	20148·0	$3^{0}_{2\frac{1}{2}}$ — $6d\ {}^{2}D_{1\frac{1}{2}}$	N	
	*	8	4855·72	20588·5	$24^{0}_{1\frac{1}{2}}$ — $9s\ {}^{2}S_{\frac{1}{2}}$	P	
	2	—	4696·25	21287·6	14^{0} — $7d\ {}^{2}D_{1\frac{1}{2}}$	N	
	*	9	60·28	21452·0	$13^{0}_{\frac{1}{2}}$ — $7d\ {}^{2}D_{1\frac{1}{2}}$	P	
	*	1	40·66	21542·6	14^{0} — $7d\ {}^{2}D_{2\frac{1}{2}}$	,,	
	1	—	4463·80	22396·2	$12^{0}_{1\frac{1}{2}}$ — $7d\ {}^{2}D_{2\frac{1}{2}}$	N	
	*	5	25·22	22591·4	$24^{0}_{1\frac{1}{2}}$ — $8d\ {}^{2}D_{1\frac{1}{2}}$	P	
	*	10	4398·62	22728·0	$24^{0}_{1\frac{1}{2}}$ — $8d\ {}^{2}D_{2\frac{1}{2}}$	,,	
	*	3	4277·80	23369·9	$21^{0}_{1\frac{1}{2}}$ — $9s\ {}^{2}S_{\frac{1}{2}}$	,,	
	*	6	4120·6	24261	$19^{0}_{\frac{1}{2}}$ — $9s\ {}^{2}S_{\frac{1}{2}}$	,,	
	3	—	4044·10	24720·4	11^{0} — $7d\ {}^{2}D_{2\frac{1}{2}}$	N	
	3	4	40·40	24743·1	$24^{0}_{1\frac{1}{2}}$ — $4_{2\frac{1}{2}}$	P	
	*	20	3983·96	25093·6	$1_{2\frac{1}{2}}$ — $6p\ {}^{2}P^{0}_{1\frac{1}{2}}$	,,	(19) *c*
	*	1	40·40	25371·0	$21^{0}_{1\frac{1}{2}}$ — $8d\ {}^{2}D_{1\frac{1}{2}}$	,,	
	*	9	18·92	25509·6	$21^{0}_{1\frac{1}{2}}$ — $8d\ {}^{2}D_{2\frac{1}{2}}$	,,	
	9	7	14·29	25540·2	$23^{0}_{3\frac{1}{2}}$ — $4_{2\frac{1}{2}}$	,,	
	3	—	3869·14	25838·1	$1^{0}_{2\frac{1}{2}}$ — $6d\ {}^{2}D_{2\frac{1}{2}}$	N	
	*	10	06·38	26264·2	$19^{0}_{\frac{1}{2}}$ — $8d\ {}^{2}D_{1\frac{1}{2}}$	P	
	*	5	3776·26	26473·7	$15^{0}_{1\frac{1}{2}}$ — $9s\ {}^{2}S_{\frac{1}{2}}$	,,	
	3	3	3632·38	27522·3	$21^{0}_{1\frac{1}{2}}$ — $4_{2\frac{1}{2}}$	,,	
	—	6	04·09	27738·4	$20^{0}_{3\frac{1}{2}}$ — $4_{2\frac{1}{2}}$	,,	
	0·5	—	3572·48	27983·8	$18^{0}_{1\frac{1}{2}}$ — $8d\ {}^{2}D_{2\frac{1}{2}}$	N	
	7	10	49·42	28165·6	$24^{0}_{1\frac{1}{2}}$ — $5_{2\frac{1}{2}}$	P	
	*	3	3510·68	28476·4	$15^{0}_{1\frac{1}{2}}$ — $8d\ {}^{2}D_{1\frac{1}{2}}$	P	
	*	7	3493·85	28613·4	$15^{0}_{1\frac{1}{2}}$ — $8d\ {}^{2}D_{2\frac{1}{2}}$	,,	

Table II—(continued).

Intensity.				λ (I.A.).	ν.	Classification.	Observer.	Remarks.
		N	P					
		*	2	84·87	28687·3	$13^0_{\frac12}$ — $9s\,{}^2S_{\frac12}$	P	
		15	10	51·69	28963·0	$23^0_{3\frac12}$ — $5_{2\frac12}$	,,	
		—	10	3385·25	29531·5	$22^0_{1\frac12}$ — $5_{2\frac12}$	,,	
		10	6	3277·87	30498·9	$16^0_{3\frac12}$ — $4_{2\frac12}$	,,	
		15	10	64·06	30627·9	$15^0_{1\frac12}$ — $4_{2\frac12}$	,,	(29·5) *c*
		*	3	57·59	30688·7	$13^0_{\frac12}$ — $8d\,{}^2D_{1\frac12}$	,,	*d*
		15	10	08·20	31161·1	$20^0_{3\frac12}$ — $5_{2\frac12}$	,,	(27) *c*
		2	—	2991·41	33419·3	$18^0_{1\frac12}$ — $5_{2\frac12}$	N	
		1	—	81·74	33527·7	$12^0_{1\frac12}$ — $4_{2\frac12}$	,,	
		20	10	47·08	33922·0	$16^0_{3\frac12}$ — $5_{2\frac12}$	P	(26) *c*
		10	0	35·92	34051·0	$15^0_{1\frac12}$ — $5_{2\frac12}$	,,	(29·5) *c*
		10	10	16·27	34280·4	$2_{1\frac12}$ — $3^0_{3\frac12}$	,,	(19) *c*
		*	10	2814·93	35514·4	$6s\,{}^2S_{\frac12}$ — $1_{2\frac12}$	,,	*b*
		5	5	06·42	35622·1	$2_{1\frac12}$ — $4^0_{1\frac12}$	,,	
		*	3	2788·40	35852·3	11^0 — $4_{2\frac12}$	,,	*a*
		1	—	69·26	36100·1	14^0 — $5_{2\frac12}$	N	
	D							
	4	8	8	05·36	36952·7	$12^0_{1\frac12}$ — $5_{2\frac12}$	P	
	—	3	2	2545·33	39275·9	11^0 — $5_{2\frac12}$	,,	
	2	2	1	23·37	39617·6	$10^0_{2\frac12}$ — $4_{2\frac12}$	,,	
	1	—	—	2499·37	39998·0	$8^0_{2\frac12}$ — $3_{3\frac12}$	D	
	5	*	5	92·09	40114·9	$7^0_{3\frac12}$ — $3_{3\frac12}$	P	*a*
	3	1	—	68·95	40490·8	$3^0_{2\frac12}$ — $7d\,{}^2D_{1\frac12}$	N	
	—	0	—	53·53	40745·2	$3^0_{2\frac12}$ — $7d\,{}^2D_{2\frac12}$	,,	
M								
5	5	8	5	14·13	41410·3	$8^0_{2\frac12}$ — $4_{2\frac12}$	P	
5	5	8	6	07·35	41526·8	$7^0_{3\frac12}$ — $4_{2\frac12}$	,,	
3	?	8	—	2345·55	42628·0	$6^0_{1\frac12}$ — $4_{2\frac12}$	N	
3	4	5	1	2339·37	42733·3	$5^0_{4\frac12}$ — $3_{3\frac12}$?	P	
—	—	0	—	22·53	43043·2	$10^0_{2\frac12}$ — $5_{2\frac12}$	N	
3	3	2	—	2296·23	43536·2	$2_{1\frac12}$ — $6^0_{1\frac12}$	,,	
5	7	10	9	62·23	44190·4	$1_{2\frac12}$ — $1^0_{2\frac12}$	P	
—	—	1	—	34·06	44747·6	$2_{1\frac12}$ — $8^0_{2\frac12}$	N	
<3	<5	1	—	29·86	44831·9	$8^0_{2\frac12}$ — $5_{2\frac12}$	,,	
—	0	2	—	24·03	44949·4	$7^0_{3\frac12}$ — $5_{2\frac12}$	,,	
3	4	—	—	2190·74	45632·4	$2_{1\frac12}$ — $9^0_{\frac12}$	D	
—	1*d*	0	—	71·07	46045·7	$6^0_{1\frac12}$ — $5_{2\frac12}$	N	
4	5	10	7	48·00	46540·2	$2_{1\frac12}$ — $10^0_{2\frac12}$	P	
8	8	10	9	2052·93	48695·3	$1_{2\frac12}$ — $2^0_{3\frac12}$	,,	(19) *c*
7	7	7	9	26·97	49318·8	$1_{2\frac12}$ — $3^0_{2\frac12}$	,,	(19·5) *c*
—	0	—	—	10·24	49729·1	$3^0_{2\frac12}$ — $8d\,{}^2D_{1\frac12}$	D	
				λ (I. vac.).				
6	6	6	8	1987·98	50304	$2_{1\frac12}$ — 11^0	P	
2	2	—	—	81·45	50468	$3^0_{2\frac12}$ — $3_{3\frac12}$	M	
4	4*d*	4	2	78·90	50533	$4^0_{1\frac12}$ — $4_{2\frac12}$	P	
—	1	—	—	77·94	50558	$6s\,{}^2S_{\frac12}$ — $2_{1\frac12}$?	D	*b*
4	4	8	5	73·89	50661	$1_{2\frac12}$ — $4^0_{1\frac12}$	P	
6	4	1	—	57·39	51088	$2^0_{3\frac12}$ — $3_{3\frac12}$	N	
4	3	3	1	27·64	51877	$3^0_{2\frac12}$ — $4_{2\frac12}$	P	
6	2	4	3	04·75	52500	$2^0_{3\frac12}$ — $4_{2\frac12}$	,,	
6	3	2	—	00·19	52626	$2_{1\frac12}$ — $12^0_{1\frac12}$	N	
5	1	*	3	1875·54	53318	$2_{1\frac12}$ — $13^0_{\frac12}$	P	
—	—	0·5	—	70·78	53482	$2_{1\frac12}$ — 14^0	N	
2		2	—	53·33	53957	$4^0_{1\frac12}$ — $5_{2\frac12}$	,,	
3		6	—	08·29	55301	$3^0_{2\frac12}$ — $5_{2\frac12}$	,,	
2		*	0·5	00·84	55530	$2_{1\frac12}$ — $15^0_{1\frac12}$	P	

Table II—(continued).

Intensity.				λ (I.A.).	ν.	Classification.	Observer.	Remarks.
M		N	P					
7		8	0·5	1798·74	55595	$1^0_{2\frac{1}{2}}$ — $3_{3\frac{1}{2}}$	P	
1		*	5	93·96	55743	$2_{1\frac{1}{2}}$ — $17^0_{\frac{1}{2}}$	,,	
0		—	—	80·00	56160	$2_{1\frac{1}{2}}$ — $18^0_{1\frac{1}{2}}$	M	
	C							
—	—	*	10	31·89	57740	$2_{1\frac{1}{2}}$ — $19^0_{\frac{1}{2}}$	P	
1	—	4	—	07·13	58578	$1_{2\frac{1}{2}}$ — $6^0_{1\frac{1}{2}}$	N	
—	—	*	7	05·52	58633	$2_{1\frac{1}{2}}$ — $21^0_{1\frac{1}{2}}$	P	
1	—	8	2	1675·90	59670	$1_{2\frac{1}{2}}$ — $7^0_{3\frac{1}{2}}$	,,	
3	—	—	7	72·62	59787	$1_{2\frac{1}{2}}$ — $8^0_{2\frac{1}{2}}$	,,	
6	2*d*	—	—	54·78	60431	$1^0_{2\frac{1}{2}}$ — $5_{2\frac{1}{2}}$	M	
0	—	*	1	28·25	61416	$2_{1\frac{1}{2}}$ — $24^0_{1\frac{1}{2}}$	P	
4	1	10	5	23·95	61578	$1_{2\frac{1}{2}}$ — $10^0_{2\frac{1}{2}}$	,,	
3	—	3	4	1530·27	65348	$1_{2\frac{1}{2}}$ — 11^0	,,	
4	—	7	4	1477·77	67669	$1_{2\frac{1}{2}}$ — $12^0_{1\frac{1}{2}}$	,,	
3	1	—	—	59·38	68522	$1_{2\frac{1}{2}}$ — 14^0	M	
10	3	*	6	17·00	70571	$1_{2\frac{1}{2}}$ — $15^0_{1\frac{1}{2}}$	P	
9	4	—	9	14·43	70700	$1_{2\frac{1}{2}}$ — $16^0_{3\frac{1}{2}}$	,,	
6	—	5	1	04·48	71201	$1_{2\frac{1}{2}}$ — $18^0_{1\frac{1}{2}}$	,,	
8	3	*	2	00·41	71408	$2_{1\frac{1}{2}}$ — $25^0_{2\frac{1}{2}}$	,,	
4	0	*	1	1372·50	72860	$2_{1\frac{1}{2}}$ — $5f\,^2F^0_{2\frac{1}{2}}$	,,	
6	2	—	9	61·31	73459	$1_{2\frac{1}{2}}$ — $20^0_{3\frac{1}{2}}$	,,	
—	—	*	5	57·32	73674	$1_{2\frac{1}{2}}$ — $21^0_{1\frac{1}{2}}$	,,	
7	1	15	10	31·76	75089	$1_{2\frac{1}{2}}$ — $22^0_{1\frac{1}{2}}$	,,	
5	1	*	10	21·73	75658	$1_{2\frac{1}{2}}$ — $23^0_{3\frac{1}{2}}$	,,	
7	1	*	9	07·95	76455	$1_{2\frac{1}{2}}$ — $24^0_{1\frac{1}{2}}$	,,	
8	1	4	—	1160·40	86177	$6s\,^2S_{\frac{1}{2}}$ — $4^0_{1\frac{1}{2}}$	N	
—	3	4	3	1062·80	94091	$6s\,^2S_{\frac{1}{2}}$ — $6^0_{1\frac{1}{2}}$	P	
4	2	2	2	39·69	96182	$6s\,^2S_{\frac{1}{2}}$ — $9^0_{\frac{1}{2}}$	,,	
2	1	4	1	969·13	103185	$6s\,^2S_{\frac{1}{2}}$ — $12^0_{1\frac{1}{2}}$	,,	
3	1	*	4	962·74	103870	$6s\,^2S_{\frac{1}{2}}$ — $13^0_{\frac{1}{2}}$	,,	
1	3	*	2	42·63	106086	$6s\,^2S_{\frac{1}{2}}$ — $15^0_{1\frac{1}{2}}$	,,	
—	—	*	6	40·79	106293	$6s\,^2S_{\frac{1}{2}}$ — $17^0_{\frac{1}{2}}$	,,	
—	1		—	37·1	106712	$6s\,^2S_{\frac{1}{2}}$ — $18^0_{1\frac{1}{2}}$	C	
—	4		4	23·39	108296	$6s\,^2S_{\frac{1}{2}}$ — $19^0_{\frac{1}{2}}$	P	
—	—		7	15·83	109191	$6s\,^2S_{\frac{1}{2}}$ — $21^0_{1\frac{1}{2}}$	,,	
—	3		—	04·2	110595	$6s\,^2S_{\frac{1}{2}}$ — $22^0_{1\frac{1}{2}}$	C	
3	2		10	893·11	111969	$6s\,^2S_{\frac{1}{2}}$ — $24^0_{1\frac{1}{2}}$	P	

* Probably observed but not recorded (see context).
P Paschen, *loc. cit.*
N Naudé, *loc. cit.*
C Carroll, *loc. cit.*
D Déjardin, ' Ann. Physik,' vol. 8, p. 424 (1927).
R Rasmussen, *loc. cit.*
M McLennan, McLay and Crawford, this investigation.
(*a*) Used by Paschen, *loc. cit.*, to evaluate 5P($9p\,^2P^0$). His values of $9p\,^2P^0$ components very questionable.
(*b*) Forbidden line.
(*c*) Excitation potential in volts observed by Déjardin (see D above).
(*d*) Classified by Paschen, *loc. cit.*, as $3P_2$—$7D_2$ ($24^0_{1\frac{1}{2}}$—$10d\,^2D_{1\frac{1}{2}}$). His values of $10d\,^2D$ components questionable.

lengths measured by the authors were observed on plates taken during our investigation of Hg III.

A more thorough interpretation of the complex term structure of Hg II than that given here may be possible when the analysis of Tl III is completed and a survey of the structures of spectra of the Au I sequence can be made more easily than at present. The important problem of quantum vector couplings in electrons of Au, Hg^+ and Tl^{++} atoms will be discussed at that time.

The Steady Broadside Motion of an Anchor Ring in an Infinite Viscous Liquid.

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Introduction and Summary.

The ring is translated along its axis of revolution with constant velocity in an infinite viscous liquid. The motion of the liquid is due to the motion of the ring, each particle moving in a meridian plane to which the vector vorticity is perpendicular. The analysis is conducted in orthogonal curvilinear "ring coordinates" using vectors, and the condition of continuity leads to a stream function which is connected with the vorticity by a partial differential equation of the second order. The equation of steady motion, on ignoring the inertia terms, is a partial differential equation of the second order in which the dependent variable is the vorticity. The motion thus comes to depend on a fourth-order partial differential equation in which the dependent variable is the stream function.

Two independent types of solution of this equation are obtained in trigonometrical series involving associated Legendre functions of degree half an odd integer, the solutions tending to zero at infinity. The arbitrary constants are determined from the boundary conditions of no slip at the surface of the ring. By means of the usual dyadics an expression is obtained for the resistance to the motion. Numerical values are omitted in the absence of the necessary tables, a defect which it is hoped to remedy in the near future.

The Coordinates.

We begin with cylindrical coordinates r, z, ϕ, in which Oz is regarded as vertical and the direction of ϕ increasing is counter-clockwise when the origin is viewed from the positive end of the z-axis. We then choose in the meridian plane two "ring coordinates," λ, θ, defined by the relation

$$\exp(\lambda - i\theta) = (b - r - iz)/(b + r + iz), \tag{1}$$

where b is some constant. The equations $\lambda = \text{const.}$, $\theta = \text{const.}$, represent two orthogonal families of coaxal circles, and the symbols involved may be interpreted as follows. Take two points A, B situate at $z = 0$, $r = \pm b$, and let P be a third point in the same meridian plane; then the angle APB $= \pi - \theta$ and $\exp\lambda = \text{PA}/\text{PB}$. The family $\lambda = \text{const.}$, has real limiting points at A, B, and the family $\theta = \text{const.}$, has real intersections at these points. The values $\exp\lambda = 0, \infty, 1$ correspond to A, B and the z-axis respectively, and as P traverses the z-axis through the z-values ∞, 0, $-\infty$ the angle θ ranges through π, 0, $-\pi$. A point at infinity is defined in general by $\theta = \pm\pi$, $\exp\lambda = 1$; the anchor ring is generated by the circle $\lambda = c$ as the meridian plane rotates about the z-axis, and it can equally well be defined by $\lambda = -c$. The expression for the arc-element is

$$\begin{aligned} ds^2 &= dz^2 + dr^2 + (r\,d\phi)^2 \\ &= r^2\{(d\lambda^2 + d\theta^2)\operatorname{cosech}^2\lambda + d\phi^2\}. \end{aligned}$$

For brevity we shall denote cosech λ by h and write

$$ds^2 = (rh)^2(d\lambda^2 + d\theta^2) + (r\,d\phi)^2 \tag{2}$$

Also

$$r = \frac{b(1 - e^{2\lambda})}{1 + 2e^{\lambda}\cos\theta + e^{2\lambda}} = -\frac{b\sinh\lambda}{\cosh\lambda + \cos\theta}$$

and

$$\left.\begin{aligned} \\ z = \frac{2be^{\lambda}\sin\theta}{1 + 2e^{\lambda}\cos\theta + e^{2\lambda}} = \frac{b\sin\theta}{\cosh\lambda + \cos\theta} \end{aligned}\right\}. \tag{3}$$

It is to be noted that h is essentially negative in the first quadrant.

The Unit Vectors.

At any point we take three unit vectors $\mathbf{l}, \mathbf{m}, \mathbf{n}$ in the direction of increasing λ, θ, ϕ respectively. The differential coefficients of these unit vectors with respect to the various coordinates are required, and, by considering the elementary rectangle whose adjacent edges are $-\mathbf{l}rh\,d\lambda$, $-\mathbf{m}rh\,d\theta$, we have from its other sides

$$\frac{\partial}{\partial\theta}(\mathbf{l}rh\,d\lambda)\,d\theta = \frac{\partial}{\partial\lambda}(\mathbf{m}rh\,d\theta)\,d\lambda$$

leading to

$$\frac{\partial\mathbf{l}}{\partial\theta} = \frac{\mathbf{m}}{rh}\frac{\partial}{\partial\lambda}(rh); \quad \frac{\partial\mathbf{m}}{\partial\lambda} = \frac{\mathbf{l}}{rh}\frac{\partial}{\partial\theta}(rh). \tag{4}$$

The condition of perpendicularity $\mathbf{l} \cdot \mathbf{m} = 0$ gives

$$\left.\begin{aligned} \frac{\partial \mathbf{l}}{\partial \lambda} &= -\frac{\mathbf{m}}{rh}\frac{\partial}{\partial \theta}(rh) \\ \frac{\partial \mathbf{m}}{\partial \theta} &= -\frac{\mathbf{l}}{rh}\frac{\partial}{\partial \lambda}(rh) \end{aligned}\right\}, \tag{5}$$

and the conditions $\mathbf{l} \cdot \mathbf{n} = 0 = \mathbf{m} \cdot \mathbf{n}$ give

$$\mathbf{l} \cdot \frac{\partial \mathbf{n}}{\partial \phi} + \mathbf{n} \cdot \frac{\partial \mathbf{l}}{\partial \phi} = 0 = \mathbf{m} \cdot \frac{\partial \mathbf{n}}{\partial \phi} + \mathbf{n} \cdot \frac{\partial \mathbf{m}}{\partial \phi}. \tag{6}$$

As $\mathbf{n}$ is perpendicular to the meridian plane we have

$$\partial \mathbf{n}/\partial \theta = 0 = \partial \mathbf{n}/\partial \lambda,$$

and the consideration of the elementary rectangle whose sides are $-\mathbf{l}\, rh\, d\lambda$ $\mathbf{n} r\, d\phi$ leads to

$$-rh\frac{\partial \mathbf{l}}{\partial \phi} = \mathbf{n}\frac{\partial r}{\partial \lambda}. \tag{7A}$$

In a similar manner we deduce

$$-rh\frac{\partial \mathbf{m}}{\partial \phi} = \mathbf{n}\frac{\partial r}{\partial \theta}. \tag{7B}$$

We also have

$$\begin{aligned} \frac{\partial \mathbf{n}}{\partial \phi} &\equiv \mathbf{l}\mathbf{l} \cdot \frac{\partial \mathbf{n}}{\partial \phi} + \mathbf{m}\mathbf{m} \cdot \frac{\partial \mathbf{n}}{\partial \phi} \\ &= -\mathbf{l}\mathbf{n} \cdot \frac{\partial \mathbf{l}}{\partial \phi} - \mathbf{m}\mathbf{n} \cdot \frac{\partial \mathbf{m}}{\partial \phi} \quad \text{by (6)}, \\ &= \frac{\mathbf{l}}{rh}\frac{\partial r}{\partial \lambda} + \frac{\mathbf{m}}{rh}\frac{\partial r}{\partial \theta}. \end{aligned} \tag{8}$$

This last result, which holds in virtue of (7), is useful as giving the inclination of the parametric curves to the horizontal and vertical.

The Stream Function.

The ring, immersed in an infinite viscous liquid, is translated along its axis of revolution with constant velocity U, so that the equatorial plane remains parallel to itself without rotation. The motion of the liquid is presumed to be due solely to the motion of the ring, each particle moving in a meridian plane and the motion being the same in all such planes.

Taking $\mathbf{v}$, with components u, v to be the velocity of any particle we have

$$\mathbf{v} = \mathbf{l}u + \mathbf{m}v \tag{9}$$

where

$$\partial u/\partial \phi = 0 = \partial v/\partial \phi. \tag{10}$$

There will exist a stream function, derivable from considerations of continuity. We have

$$\frac{\partial}{\partial\theta}(2\pi r\,.\,v\,.\,rh\,d\lambda)\,d\theta+\frac{\partial}{\partial\lambda}(2\pi r\,.\,u\,.\,rh\,d\theta)\,d\lambda=0$$

leading to

$$v=-\frac{1}{r^2h}\frac{\partial\psi}{\partial\lambda},\quad u=\frac{1}{r^2h}\frac{\partial\psi}{\partial\theta}. \tag{11}$$

The Boundary Conditions.

Assuming the absence of slip at the surface of the ring, we can utilise (8) to effect the tangential and normal resolution of the velocity U, and so derive the relations

$$u=\frac{1}{r^2h}\frac{\partial\psi}{\partial\theta}=-\frac{\mathrm{U}}{rh}\frac{\partial r}{\partial\theta},$$

$$v=-\frac{1}{r^2h}\frac{\partial\psi}{\partial\lambda}=\frac{\mathrm{U}}{rh}\frac{\partial r}{\partial\lambda}.$$

These can be written

$$\partial\mathrm{R}/\partial\theta=0=\partial\mathrm{R}/\partial\lambda \tag{12}$$

where

$$\mathrm{R}=\psi+\tfrac{1}{2}\mathrm{U}r^2.$$

They will subsequently be used in slightly different but equivalent forms.

The Vorticity.

In motion of the type at present under consideration, the vorticity $\mathbf{w}$ is evidently perpendicular to the meridian plane, so that $\mathbf{w}=\mathbf{n}w$. For the evaluation of w we have

$$\mathbf{w}=\operatorname{curl}\mathbf{v}=\left(-\frac{\mathbf{l}}{rh}\cdot\frac{\partial}{\partial\lambda}-\frac{\mathbf{m}}{rh}\cdot\frac{\partial}{\partial\theta}+\frac{\mathbf{n}}{r}\cdot\frac{\partial}{\partial\phi}\right)\wedge(\mathbf{l}u+\mathbf{m}v),$$

$$=-\frac{\mathbf{l}}{rh}\wedge\left(u\frac{\partial\mathbf{l}}{\partial\lambda}+\mathbf{m}\frac{\partial v}{\partial\lambda}\right)-\frac{\mathbf{m}}{rh}\wedge\left(\mathbf{l}\frac{\partial u}{\partial\theta}+v\frac{\partial\mathbf{m}}{\partial\theta}\right),$$

the rest vanishing in virtue of (4) and (7). By the use of (5) this becomes

$$\mathbf{w}=\frac{\mathbf{n}}{rh}\left\{\frac{\partial u}{\partial\theta}-\frac{\partial v}{\partial\lambda}+\frac{v}{rh}\frac{\partial(rh)}{\partial\lambda}-\frac{u}{rh}\frac{\partial(rh)}{\partial\theta}\right\}$$

$$=\frac{\mathbf{n}}{r^2h^2}\left\{\frac{\partial(urh)}{\partial\theta}-\frac{\partial(vrh)}{\partial\lambda}\right\}.$$

Inserting the values of u, v from (11), we have as the connection between the vorticity and the stream function

$$\mathbf{n}w=\mathbf{w}=\frac{\mathbf{n}}{r^2h^2}\left\{\frac{\partial}{\partial\lambda}\left(\frac{1}{r}\cdot\frac{\partial\psi}{\partial\lambda}\right)+\frac{\partial}{\partial\theta}\left(\frac{1}{r}\cdot\frac{\partial\psi}{\partial\theta}\right)\right\}. \tag{13}$$

The Steady Motion.

For steady motion in the absence of body forces the equation of motion for the liquid is

$$\nu\nabla^2\mathbf{v} - \frac{1}{\rho}\nabla p = \mathbf{v}\,.\,\nabla\mathbf{v}\,,$$

where p is the pressure, ρ the density and ν the kinematical viscosity. If we assume that the motion is slow enough to permit the ignoration of the inertia terms on the right, and we take the curl of the left side, we have $\nabla^2\mathbf{w} = 0$. As $\mathbf{w} = \mathbf{n}w$ with $\partial w/\partial\phi = 0$, it is known* that we can write this as

$$\nabla^2\mathbf{w} = \frac{\mathbf{n}}{r^3h^2}\left\{\frac{\partial}{\partial\lambda}\left(r\frac{\partial w}{\partial\lambda}\right) + \frac{\partial}{\partial\theta}\left(r\frac{\partial w}{\partial\theta}\right) - rh^2w\right\}$$

$$= \mathbf{n}\,(\nabla^2 w - w/r^2) = 0. \tag{14}$$

Here we can insert the value of w from (13), giving the equation of motion in terms of the stream function as a partial differential equation of the fourth order.

Modification of the Equation of Motion.

The substitution $wr^{\frac{1}{2}} = \xi$ converts (14) to the form

$$\frac{\partial^2\xi}{\partial\lambda^2} + \frac{\partial^2\xi}{\partial\theta^2} - \tfrac{3}{4}h^2\xi = 0. \tag{15}$$

This suggests that a suitable modification for (13) might be $\psi = r^{\frac{1}{2}}\chi$. On trying it out, it is easily verified that

$$\frac{\partial}{\partial\lambda}\left\{\frac{1}{r}\frac{\partial}{\partial\lambda}(r^{\frac{1}{2}}\chi)\right\} = r^{-\frac{1}{2}}\left\{\frac{\partial^2\chi}{\partial\lambda^2} + \frac{\chi}{2r}\frac{\partial^2 r}{\partial\lambda^2} - \tfrac{3}{4}\chi\left(\frac{\partial}{\partial\lambda}\log r\right)^2\right\}, \tag{16}$$

and a similar equation holds wherein θ replaces λ.

From the invariance of ∇^2 it follows that, to a factor près, $\partial^2/\partial\lambda^2 + \partial^2/\partial\theta^2$ is equivalent to $\partial^2/\partial r^2 + \partial^2/\partial z^2$ when applied to r and gives zero. Moreover, from (3) we get after a little reduction

$$\left(\frac{\partial}{\partial\lambda}\log r\right)^2 + \left(\frac{\partial}{\partial\theta}\log r\right)^2 = h^2, \tag{17}$$

so that (17), (16) and its congener in θ show that (13) can be written

$$wr^{\frac{1}{2}} = \frac{1}{r^2h^2}\left\{\frac{\partial^2\chi}{\partial\lambda^2} + \frac{\partial^2\chi}{\partial\theta^2} - \tfrac{3}{4}h^2\chi\right\} = \xi. \tag{18}$$

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* Phil. Mag., vol. 11, p. 132 (1931).

Utilising this value of ξ in (15), we see that the determination of the motion comes to depend upon the solution of the equation

$$\left(\frac{\partial^2}{\partial\lambda^2}+\frac{\partial^2}{\partial\theta^2}-\tfrac{3}{4}\operatorname{cosech}^2\lambda\right)\left\{(\cosh\lambda+\cos\theta)^2\left(\frac{\partial^2\chi}{\partial\lambda^2}+\frac{\partial^2\chi}{\partial\theta^2}-\tfrac{3}{4}\chi\operatorname{cosech}^2\lambda\right)\right\}=0. \quad (19)$$

The Solution of the Equation.

The equation

$$\frac{\partial^2\chi}{\partial\lambda^2}+\frac{\partial^2\chi}{\partial\theta^2}-\tfrac{3}{4}\chi\operatorname{cosech}^2\lambda=0 \quad (20)$$

manifestly has solutions of the type $\chi = \mathrm{L}\exp ik\theta = \mathrm{F}(\lambda)\exp ik\theta$, where L is determined from

$$\frac{d^2\mathrm{L}}{d\lambda^2}-(k^2+\tfrac{3}{4}h^2)\,\mathrm{L}=0. \quad (21)$$

This last equation I have solved elsewhere* in terms of Riemann's P-function; but for our present purpose we change the independent variable to $\nu = \cosh\lambda$. We then have

$$(\nu^2-1)\frac{d^2\mathrm{L}}{d\nu^2}+\nu\frac{d\mathrm{L}}{d\nu}-\left\{k^2+\frac{3}{4(\nu^2-1)}\right\}\mathrm{L}=0, \quad (22)$$

which is evidently closely related to the equation for associated Legendre functions. If we put $\mathrm{L}=(\nu^2-1)^{\frac{1}{4}}\,\mathrm{M}$ it becomes

$$(1-\nu^2)\frac{d^2\mathrm{M}}{d\nu^2}-2\nu\frac{d\mathrm{M}}{d\nu}+\left\{(k^2-\tfrac{1}{4})-\frac{1}{1-\nu^2}\right\}\mathrm{M}=0, \quad (23)$$

of which the solution is

$$\mathrm{M}=\mathrm{P}^1{}_{k-\frac{1}{2}}(\nu).$$

It follows that solutions of (19) and (20) are

$$a_k(\nu^2-1)^{\frac{1}{4}}\,\mathrm{P}^1{}_{k-\frac{1}{2}}(\nu)\,{\sin\atop\cos}\,k\theta \quad (24)$$

where a_k is arbitrary. These solutions tend to zero at infinity, where $\nu = \exp\lambda = 1$.

For the purpose of getting other and independent solutions of (19) we evaluate the left side of (20) on the assumption that $\chi = \mathrm{Y}z$. We thus have

$$\frac{\partial^2\chi}{\partial\lambda^2}+\frac{\partial^2\chi}{\partial\theta^2}-\tfrac{3}{4}h^2\chi\equiv\mathrm{Y}\left(\frac{\partial^2 z}{\partial\lambda^2}+\frac{\partial^2 z}{\partial\theta^2}\right)+z\left(\frac{\partial^2\mathrm{Y}}{\partial\lambda^2}+\frac{\partial^2\mathrm{Y}}{\partial\theta^2}-\tfrac{3}{4}h^2\mathrm{Y}\right)$$
$$+2\left(\frac{\partial\mathrm{Y}}{\partial\lambda}\cdot\frac{\partial z}{\partial\lambda}+\frac{\partial\mathrm{Y}}{\partial\theta}\cdot\frac{\partial z}{\partial\theta}\right).$$

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* *Loc. cit.*

The first bracket on the right is manifestly zero, due to the invariance of ∇^2. The second bracket on the right will be zero if Y is taken to be a solution of (20). Hence on this assumption we have

$$(\cosh\lambda+\cos\theta)^2\left(\frac{\partial^2\chi}{\partial\lambda^2}+\frac{\partial^2\chi}{\partial\theta^2}-\tfrac{3}{4}h^2\chi\right)$$
$$=2b\left\{(1+\cos\theta\cosh\lambda)\frac{\partial \mathrm{Y}}{\partial\theta}-\sin\theta\sinh\lambda\frac{\partial \mathrm{Y}}{\partial\lambda}\right\}.$$

It is then a matter of simple substitution to verify that the right-hand side of this last equation is a solution of (20), which shows that $\mathrm{Y}z$ is a solution of (19) if Y is a solution of (20). We accordingly have as solutions of (19)

$$b_k(\nu^2-1)^{\frac{1}{2}}\,\mathrm{P}^1{}_{k-\frac{1}{2}}(\nu)\sin\theta\,{}^{\sin}_{\cos}\,k\theta/(\nu+\cos\theta), \tag{25}$$

which tend to zero when $\nu=1$. Remembering that $\psi=r^{\frac{1}{2}}\chi$, we have as a possible form of the stream function

$$\psi=\Sigma_k\left(a_k\cos k\theta+b_k\frac{\sin\theta\sin k\theta}{\nu+\cos\theta}\right)\frac{\sinh\lambda}{(\nu+\cos\theta)^{\frac{1}{2}}}\,\mathrm{P}^1{}_{k-\frac{1}{2}}(\nu), \tag{26}$$

where an even function of θ has been chosen, in consonance with (11), and the constants are yet to be determined.

The Determination of the Constants.

In future we shall denote the awkward suffix $k-\frac{1}{2}$ by the single letter j, so that (26) reads

$$\psi=\frac{\sinh\lambda}{(\nu+\cos\theta)^{3/2}}\Sigma_k\{a_k(\nu+\cos\theta)\cos k\theta+b_k\sin\theta\sin k\theta\}\,\mathrm{P}^1{}_j(\nu). \tag{27}$$

The boundary conditions (12) will be replaced by the equivalent statement that

$$\mathrm{R}\,(\nu+\cos\theta)^{3/2}/(\nu^2-1),$$

together with its first differential coefficient with respect to λ, shall be zero at the surface of the ring.

If we pick out the coefficient of $\cos k\theta$ from under the summation sign in (27), we have

$$a_k\nu\mathrm{P}^1{}_j(\nu)+\tfrac{1}{2}\left(a_{k+1}\mathrm{P}^1{}_{j+1}(\nu)+a_{k-1}\mathrm{P}^1{}_{j-1}(\nu)\right)+\tfrac{1}{2}\left(b_{k+1}\mathrm{P}^1{}_{j+1}(\nu)-b_{k-1}\mathrm{P}^1{}_{j-1}(\nu)\right).$$

The recurrence relation

$$j\mathrm{P}^1{}_{j+1}(\nu)-(2j+1)\,\nu\mathrm{P}^1{}_j(\nu)+(j+1)\,\mathrm{P}^1{}_{j-1}(\nu)=0$$

enables us to write this coefficient as

$$\sinh\lambda\,\{\mathrm{A}_k\mathrm{P}'{}_{j+1}(\nu)+\mathrm{B}_k\mathrm{P}'{}_{j-1}(\nu)\},$$

where primes denote differentiation with respect to ν, so that (27) now runs

$$\psi = (\nu^2 - 1)(\nu + \cos\theta)^{-3/2}\Sigma_k\{A_k P'_{j+1}(\nu) + B_k P'_{j-1}(\nu)\}\cos k\theta. \qquad (28)$$

This implies that

$$\Sigma_k\{A_k P'_{j+1}(\nu) + B_k P'_{j-1}(\nu)\}\cos k\theta + \tfrac{1}{2}Ub^2(\nu + \cos\theta)^{-\frac{1}{2}},$$

together with its first differential coefficient with respect to λ or ν, is zero at the surface of the ring. Now for $(\nu + \cos\theta)^{-\frac{1}{2}}$ we have a Fourier expansion in which the coefficient of $\cos k\theta$ is $(-)^k 2^{3/2}\pi^{-1}Q_j(\nu)$, so that our constants are determined from the equations

$$\left.\begin{aligned} A_k P'_{j+1} + B_k P'_{j-1} + (-)^k 2^{\frac{1}{2}}\pi^{-1}Ub^2 Q_j &= 0 \\ A_k P''_{j+1} + B_k P''_{j-1} + (-)^k 2^{\frac{1}{2}}\pi^{-1}Ub^2 Q'_j &= 0 \end{aligned}\right\}, \qquad (29)$$

whence we have

$$\frac{A_k}{P'_{j-1}Q'_j - P''_{j-1}Q_j} = \frac{B_k}{P''_{j+1}Q_j - P'_{j+1}Q'_j} = \frac{(-)^k 2^{\frac{1}{2}}\pi^{-1}Ub^2}{P'_{j+1}P''_{j-1} - P''_{j+1}P'_{j-1}}, \qquad (30)$$

where the omitted argument of the Legendre functions is $\alpha = \cosh c$ in every case. The stream function (28) is now completely determined, as also is the velocity in accordance with (11), and the vorticity in accordance with (13).

The Pressure Distribution.

In view of our present assumption that the inertia terms are ignorable, the equation for the steady motion takes the form

$$\frac{1}{\rho}\nabla p = \nu\nabla^2\mathbf{v}.$$

Now

$$\begin{aligned} \nabla\wedge\mathbf{w} &= \nabla\wedge\nabla\wedge\mathbf{v} \\ &= \nabla\nabla\cdot\mathbf{v} - \nabla^2\mathbf{v} \\ &= -\nabla^2\mathbf{v}, \end{aligned}$$

since $\nabla\cdot\mathbf{v} \equiv 0$ by the equation of continuity. The equation for the pressure becomes

$$\frac{1}{\mu}\nabla p = -\nabla\wedge\mathbf{w},$$

$$\frac{1}{\mu}\left(\frac{\mathbf{l}}{rh}\cdot\frac{\partial p}{\partial\lambda} + \frac{\mathbf{m}}{rh}\cdot\frac{\partial p}{\partial\theta} - \frac{\mathbf{n}}{r}\cdot\frac{\partial p}{\partial\phi}\right) = -\left(\frac{\mathbf{l}}{rh}\cdot\frac{\partial}{\partial\lambda} + \frac{\mathbf{m}}{rh}\cdot\frac{\partial}{\partial\theta} - \frac{\mathbf{n}}{r}\cdot\frac{\partial}{\partial\phi}\right)\wedge\mathbf{n}w$$

$$= -\frac{\mathbf{l}}{r^2h}\cdot\frac{\partial(wr)}{\partial\theta} + \frac{\mathbf{m}}{r^2h}\cdot\frac{\partial(wr)}{\partial\lambda}.$$

Thus $\partial p/\partial \phi$ is zero, as we should naturally expect, and

$$\frac{1}{\mu}\cdot\frac{\partial p}{\partial \lambda} = -\frac{1}{r}\cdot\frac{\partial (wr)}{\partial \theta}, \quad \frac{1}{\mu}\frac{\partial p}{\partial \theta} = \frac{1}{r}\cdot\frac{\partial (wr)}{\partial \lambda}. \tag{31}$$

Accordingly, a necessary relation, obtained by eliminating p, is that

$$\frac{\partial}{\partial \lambda}\left\{\frac{1}{r}\cdot\frac{\partial (wr)}{\partial \lambda}\right\} + \frac{\partial}{\partial \theta}\left\{\frac{1}{r}\cdot\frac{\partial (wr)}{\partial \theta}\right\} = 0,$$

and it can be readily verified from (14) that this relation holds good.

The Resistance.

For the stress dyadic we have

$$\Psi = \Sigma\, \mathrm{T}_{11}\, \mathbf{ll} + \Sigma\, \mathrm{T}_{12}\, (\mathbf{lm} + \mathbf{ml}), \tag{32}$$

and for the self-conjugate part of the rate-of-strain dyadic we have

$$\Phi = \tfrac{1}{2}\, (\nabla \mathbf{v} + \mathbf{v} \nabla), \tag{33}$$

where

$$\nabla \mathbf{v} = \left(-\frac{\mathbf{l}}{rh}\cdot\frac{\partial}{\partial \lambda} - \frac{\mathbf{m}}{rh}\cdot\frac{\partial}{\partial \theta} + \frac{\mathbf{n}}{r}\cdot\frac{\partial}{\partial \phi}\right)(\mathbf{l}u + \mathbf{m}v).$$

From this it follows that

$$\Phi = \mathbf{ll}\left\{v\frac{\partial}{\partial \theta}\left(\frac{1}{rh}\right) - \frac{1}{rh}\cdot\frac{\partial u}{\partial \lambda}\right\} + \mathbf{mm}\left\{u\frac{\partial}{\partial \lambda}\left(\frac{1}{rh}\right) - \frac{1}{rh}\cdot\frac{\partial v}{\partial \theta}\right\}$$
$$- \mathbf{nn}\left\{v\,\frac{\partial r}{\partial \theta} + u\frac{\partial r}{\partial \lambda}\right\}\frac{1}{r^2 h} - \tfrac{1}{2}\,(\mathbf{lm} + \mathbf{ml})\left\{\frac{\partial}{\partial \lambda}\left(\frac{v}{rh}\right) + \frac{\partial}{\partial \theta}\left(\frac{u}{rh}\right)\right\}. \tag{34}$$

It will be observed that, in accordance with expectation, only one shear is present.

In the absence of dilatation we have as the linear connection between the dyadics

$$\Psi = -p\mathrm{I} + 2\mu\Phi \tag{35}$$

where I is the idem factor, so that

$$\left.\begin{aligned} \mathrm{T}_{11} &= -p + 2\mu\left\{v\,\frac{\partial}{\partial \theta}\left(\frac{1}{rh}\right) - \frac{1}{rh}\cdot\frac{\partial u}{\partial \lambda}\right\} \\ \mathrm{T}_{12} &= -\mu\left\{\frac{\partial}{\partial \lambda}\left(\frac{v}{rh}\right) + \frac{\partial}{\partial \theta}\left(\frac{u}{rh}\right)\right\} \\ \mathrm{T}_{13} &= 0. \end{aligned}\right\} \tag{36}$$

In order to get the force on the ring we note that the stress across a plane normal to $\mathbf{l}$ is

$$\mathbf{l}\,.\,\Psi = \mathbf{l}\mathrm{T}_{11} + \mathbf{m}\mathrm{T}_{12} + \mathbf{n}\,\mathrm{T}_{13}.$$

We see from (8) that the vertically downward resolute of this is

$$\frac{1}{rh}\left(\mathrm{T}_{11}\frac{\partial r}{\partial\theta}-\mathrm{T}_{12}\frac{\partial r}{\partial\lambda}\right),$$

giving as the resistance

$$\int_{-\pi}^{\pi}\frac{1}{rh}\left(\mathrm{T}_{12}\frac{\partial r}{\partial\lambda}-\mathrm{T}_{11}\frac{\partial r}{\partial\theta}\right)2\pi r\,.\,rh\,d\theta$$

$$=2\pi\int_{-\pi}^{\pi}pr\frac{\partial r}{\partial\theta}\,.\,d\theta-4\pi\mu\int_{-\pi}^{\pi}\left\{v\frac{\partial}{\partial\theta}\left(\frac{1}{rh}\right)-\frac{1}{rh}\frac{\partial u}{\partial\lambda}\right\}r\frac{\partial r}{\partial\theta}\,.\,d\theta$$

$$-2\pi\mu\int_{-\pi}^{\pi}\left\{\frac{\partial}{\partial\lambda}\left(\frac{v}{rh}\right)+\frac{\partial}{\partial\theta}\left(\frac{u}{rh}\right)\right\}r\frac{\partial r}{\partial\lambda}\,d\theta. \qquad (37)$$

The first of these three terms admits of an obvious integration by parts, and the utilisation of (31) enables us to write it as

$$-\pi\mu\int_{-\pi}^{\pi}r\frac{\partial}{\partial\lambda}(wr)\,d\theta.$$

The evaluation of these various integrals by the use of (28), (13) and (11) depends upon the integral*

$$\int_{-\pi}^{\pi}\frac{\cos m\theta}{(\nu+\cos\theta)^{n+\frac{1}{2}}}\,d\theta=(-)^{m-n}\frac{2^{3/2}\pi}{\Gamma(\frac{1}{2})\,\Gamma(n+\frac{1}{2})}(\nu^2-1)^{-\frac{1}{2}n}\,\mathrm{Q}^{n}{}_{m-\frac{1}{2}}(\nu). \qquad (40)$$

Owing to the large number of reduction formulæ for the Legendre and associated functions, the final result can be expressed in a variety of forms. Perhaps the most symmetrical is

$$8\mu\mathrm{U}b\sum_{k=0}^{\infty}(\mathrm{E}_k+\mathrm{F}_k+\mathrm{G}_{\mathrm{G}}),$$

where E, F, G are numbers whose values are given as follows. The ring being defined by $\lambda=c$, we use as convenient abbreviations $\alpha=\cosh c$, $\beta=\sinh c$; omitting the argument of the Legendre functions, which in every case is α, we have

$$\mathrm{E}_k=k\beta^4\mathrm{Q}_j\,\frac{\mathrm{P}^2{}_{j+1}\mathrm{Q}^1{}_j\mathrm{P}^1{}_{j-1}-2\mathrm{P}^2{}_{j+1}\mathrm{Q}_j\mathrm{P}^2{}_{j-1}+\mathrm{P}^2{}_{j-1}\mathrm{Q}^1{}_j\mathrm{P}^1{}_{j+1}}{\mathrm{P}^2{}_{j+1}\mathrm{P}^1{}_{j-1}-\mathrm{P}^1{}_{j+1}\mathrm{P}^2{}_{j-1}}$$

$$\mathrm{F}_k=k\beta^3\mathrm{Q}^1{}_j\,\frac{\mathrm{P}^2{}_{j+1}\mathrm{Q}_j\mathrm{P}^1{}_{j-1}-2\mathrm{P}^1{}_{j+1}\mathrm{Q}^1{}_j\mathrm{P}^1{}_{j-1}+\mathrm{P}^1{}_{j+1}\mathrm{Q}_j\mathrm{P}^2{}_{j-1}}{\mathrm{P}^2{}_{j+1}\mathrm{P}^1{}_{j-1}-\mathrm{P}^1{}_{j+1}\mathrm{P}^2{}_{j-1}}$$

$$\mathrm{G}_k=\alpha\beta^2\left(\tfrac{9}{5}k^2\mathrm{Q}_j\mathrm{Q}_j-\mathrm{Q}^1{}_j\mathrm{Q}^1{}_j\right)-\tfrac{1}{1}\,\beta^4(4k^2-1)(2k^2+7)\,\mathrm{Q}_j(\mathrm{Q}_{j+1}+\mathrm{Q}_{j-1}).$$

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* A proof of this result, which appears to be new, will appear shortly in the 'Journal Lond. Math. Soc.'

In conclusion, we may remark that the constants b, c which determine the size of the ring are connected with the usual dimensions by the fact that if D, d are the external and internal diameters respectively, we have

$$D = -2b \coth \tfrac{1}{2}c, \quad d = -2b \tanh \tfrac{1}{2}c.$$

As soon as possible, the necessary tables for associated Legendre functions, of degree half an odd integer, will be computed. I will then, in a future paper, give numerical illustrations of the foregoing results.

The Thermal Conductivities of Certain Approximately Pure Metals and Alloys at High Temperatures.

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Introduction.

Measurements have been made by several observers on the thermal conductivities of metals and alloys up to high temperatures. Heat losses to the surroundings become large at high temperatures, hence the guard tube method, which to a great extent eliminates these losses, has been popular for work at these temperatures. This method was described and used by Berget[*] in 1888, and later by Wilkes.[†] These observers measured the rate of heat flow by a calorimetric method, which is not suitable for work at high temperatures. Honda and Simidu,[‡] using an internal heating coil, determined the heat flow from the energy input and were able to obtain results for nickel and steel to over 800° C. More recently, Schofield,[§] using the guard tube method with an internal heating coil, has obtained results up to a maximum temperature of 700° C. with five metals.

The present work was undertaken with a view to continuing the work of Professor C. H. Lees[||] on the effect of temperatures between —160° C. and 15° C. on the thermal conductivities of nine metals and six alloys.

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[*] Berget, 'J. Physique,' vol. 7, p. 503 (1888).

[†] Wilkes, 'Chem. Met. Engineering,' vol. 21, p. 241 (1919).

[‡] K. Honda and T. Simidu, 'Sc. Rep. Tohoku Univ.,' vol. 6, p. 219 (1917).

[§] F. H. Schofield, 'Proc. Roy. Soc.,' A, vol. 107, p. 206 (1925).

[||] C. H. Lees, 'Phil. Trans.,' A, vol. 208, p. 381 (1908).

In the present experiments, the same specimens were used, and the conductivities of metals and alloys measured from about 60° C. to a maximum of 550° C., the guard tube method being employed.

The Apparatus.

The metal rods R (fig. 1) were circular cylinders 7 to 8 cm. long, 0·585 cm. in diameter, accurately turned out of larger rods. Their lower ends fitted into a copper disc, D, of 2·3 cm. diameter, 1·2 cm. thick in the centre, 1 cm. thick at the circumference, which itself fitted into a steel cylinder T, 10 cm. long, 2·5 cm. external diameter, closed at the top with a copper disc which could be removed at will.

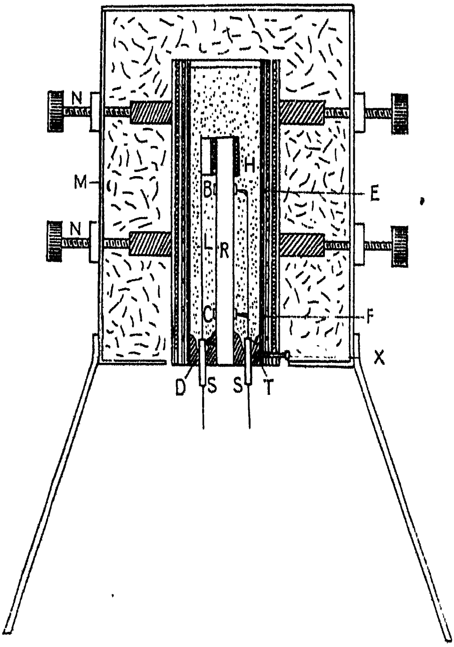

Fig. 1.—Apparatus.

The heating coils, H, were wound directly on the upper end of each rod, on a very thin (0·002 cm.) mica sleeve, 1·3 to 1·5 cm. long, and consisted of 15 to 20 turns of No. 36 bare nichrome wire, kept in position by a thin covering of alundum cement. The ends of the nichrome wires, about 1 cm. long, were hard soldered to No. 22 gauge copper leads, L.

The temperature of the rod was measured at two points, B and C, on the rod, by thermocouples hard soldered to thin copper sleeves, 0·30 cm. long, and 0·03 cm. thick, on the rods at these points. The sleeves, which were electrically insulated from the rod by thin (0·002 cm.) mica sleeves, fitted the rods fairly tightly, but could be slid off without damaging them.

The copper leads from the heating coil and the four wires from the hot junctions of the thermocouples passed out of the apparatus through small silica capillary tubes, S, cemented into the copper disc.

The guard tube was of steel, of thermal conductivity 0·11, so that a thermal gradient was easily obtained down the tube. Two screws, X, near the lower end of the tube served to fix the rod and copper disc in position. Thermocouples of "chromel-alumel" were hard soldered to the outside of the guard tube at four points, two of these, E, F, corresponding in position to those on the rods; the other two being used only to test the temperature distribution along the tube.

Two heating coils were wound on the guard tube, insulated from it and from each other by asbestos paper.

The inner coil, of about 500 ohms resistance, consisted of No. 36 bare nichrome wire. To produce an approximately linear thermal gradient down the tube the majority of the wire was wound on the upper part of the tube corresponding to the heating coil on the rod, and a few turns were wound on the remainder of the tube to balance the lateral heat loss from the tube. The outer coil, of about 700 ohms resistance, was uniformly wound with No. 36 bare nichrome wire, and served to raise the temperature of the whole apparatus. All wires from both heating coils and thermocouples on the guard tube were taken out at the top of the tube through silica or pyrex glass tubes.

The space between the rod and the guard tube was packed with powdered magnesia, to prevent convection currents and to reduce oxidation of the specimens.

The whole apparatus was supported vertically in a large cylindrical metal vessel, M, by two sets of three screws, N, one set being vertically above the other. The screws had end pieces of sandanayo, a heat-insulating material which could be worked, to reduce any heat losses along the screws. The space between the guard tube and the walls of the vessel was packed with asbestos wool to reduce heat losses.

The Electric Circuits.

Power was supplied to the heating coil on the rod from storage cells at 100 volts, the current and potential difference across the coil being measured to obtain the energy input to the rod. Power was supplied to the coils on the guard tube from 240-volt lighting mains.

The current was measured by a calibrated ammeter, and the potential difference on the thermo-electric potentiometer, a volt box being used to reduce its value to one ten-thousandth of its real value.

The thermocouples used were of the alloy combination "chromel-alumel" (chromel = 90 Ni, 10 Cr; alumel = 98 Al, 2 Ni + Sn and Mn) which combination was found to give a linear e.m.f.-temperature relation over a wide range of temperature. The couples did not appear to change their properties appreciably with time and heat treatment, and different couples gave at the same temperatures e.m.fs. which differed but slightly.

The hot junctions on the rod were hard soldered to the copper sleeves, those on the guard tube directly soldered to its outer surface. Each cold junction was placed in a sealed glass tube containing mercury, the glass tube being placed in a large jacketed vessel containing water at the room temperature. The temperature of the cold junctions was measured with a thermometer graduated in 0·1 degrees, readings being corrected to a standard cold junction temperature of 20° C. The extremes of cold junction temperature were 16° C. and 25° C., the usual daily variation being about 2° C.

The thermocouples were calibrated by measuring the e.m.fs. generated when the hot junctions were at the temperature of melting ice, steam, aniline vapour, benzophenone vapour, and sulphur vapour, the cold junctions being maintained near 20° C. Measurements with different couples gave results in close agreement, the thermo-electric power being 41·3 micro-volts per degree. Precautions were taken to insulate the thermocouples from one another and from the heating circuits, so that leaks were prevented.

The potentiometer was arranged as shown in fig. 2. The main circuit

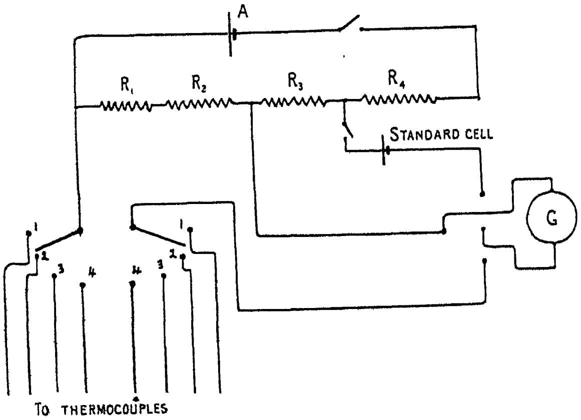

FIG. 2.—Potentiometer.

consisted of an accumulator A, and resistances R_1, R_2, R_3, R_4 in series. The resistance R_3 was kept constant at 5091·5 ohms and the potential drop across it balanced against the electromotive force of a standard cadmium cell of e.m.f. 1·0183 volt at 18° C., by varying the main circuit current. The current was thus kept constant at 2×10^{-4} ampere.

When balancing the e.m.f. of a thermocouple, the resistances of R_1 and R_2 were varied. R_2 varied from 0·01 ohm in steps of 0·01 ohm up to 1 ohm, while R_2 varied from 1 ohm to 11,000 ohms, while R_4 consisted of about 5000 ohms resistance, which was varied to keep the main current constant. In general, measurements were made to 0·01 ohm, equivalent to 2 microvolts, but the e.m.f. could be judged to 1 microvolt if desired. Before measuring an e.m.f., the main circuit current was set to the standard value by balancing against the standard cell. The various thermocouples were connected to the potentiometer by the mercury switch M.

Method of Experiment.

For each rod used a separate heating coil was wound, and the copper leads hard soldered to the ends of the nichrome wire. The copper sleeves with their attached thermocouples were then fixed in position on the rod so that their positions would correspond with those on the guard tube in the assembled apparatus ; after which the lower end of the rod was fixed in the copper disc, D, and the heating coil and thermocouple wires passed through the disc and fixed in position. The rod and disc were then slid up into the guard tube until the lower ends of rod, disc, and guard tube were flush, when the screws holding the disc in position were tightened.

Heat was supplied to the rod and guard tube, the temperature gradient along the guard tube being varied by varying the current through the inner coil, and the temperature of the whole being varied by varying the current through the outer coil, until a final steady state was reached where the temperature at the two points on the rod and guard tube agreed to within about 1° C. In this case, if the distribution along the guard tube were linear, the temperatures at corresponding points along the rod and tube would be nearly equal, and lateral losses would be very small. It was sometimes found better to vary the heat input to the rod, keeping the guard tube currents constant, till the temperatures of rod and tube agreed, rather than vary the heat input to the tube. When commencing a series of readings, 1½ to 2 hours were allowed to elapse before any steady-state readings were taken ; after this further readings could be taken at intervals of an hour. Series of steady-state readings were taken with the average temperature of the rod both increasing and decreasing.

Theory of the Method.

If a rod of the metal or alloy be used with a guard tube so that the temperatures at all points along both rod and guard tube are equal, then lateral heat losses are prevented, and the gradient becomes very approximately linear, the equation

$$H_0 = qk\frac{(v_B - v_A)}{(x_B - x_A)}, \tag{1}$$

being nearly true, where H_0 is the heat flow down the rod in calories per second; q the cross-sectional area of the rod; k the thermal conductivity of the rod; v_B, v_A, the temperatures at two points distant x_B, x_A cm., respectively, from the lower end of the rod. The gradient would only be linear if there were no lateral heat losses, if the conductivity of the metal were constant, and if the heat source were of zero thickness.

The temperatures of the rod and guard tube were automatically equal at their lower ends, and were made equal at two other points. A separate investigation* showed the temperature distribution along the rod and guard tube to be in close agreement, hence lateral heat losses were very small, and equation (1) was very nearly obeyed.

Effect of the Sleeves.

(*a*) *Heating Coil Sleeve.*—On account of the fact that the heat entered the rod over the curved surface of a mica sleeve on the upper end of the rod, the isothermal surfaces in the rod were not accurately planes perpendicular to the axis. It has, however,† been shown that the effect is negligible for rods of the dimensions used.

(*b*) *Thermocouple Sleeves.*—It has been shown† that the variation of temperature along the rod and sleeve in a portion of rod covered by sleeve is given by

$$(qk + q'k')\,v = H_0\left\{x + \frac{q'k'}{qk}\cdot\frac{1}{\alpha}\cdot\frac{\sinh\alpha x}{\cosh\alpha b}\right\}, \tag{2}$$

$$(qk + q'k')\,v' = H_0\left\{x - \frac{q'k'}{qk}\cdot\frac{1}{\alpha}\cdot\frac{\sinh\alpha x}{\cosh\alpha b}\right\}, \tag{3}$$

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* See p. 67.

† C. L. Lees, *loc. cit.*

if the origin of x be taken at the central transverse section, the temperature then be taken as zero, and where H_0 is the heat flow; where v, q, k, v', q', k', have the usual meanings for rod and sleeve respectively, b is the half length of the sleeve, and

$$\alpha^2 = \frac{pk''}{t''}\left\{\frac{1}{qk} + \frac{1}{q'k'}\right\}.$$

If b' = the length of free rod equivalent in thermal resistance to the length b of rod enclosed by sleeve, we have

$$b' = b \cdot \frac{qk}{qk + q'k'}\left\{1 + \frac{q'k'}{qk}\frac{\tanh \alpha b}{\alpha b}\right\}. \tag{4}$$

The first term on the right is the correction due to the increase of cross section at the sleeve, and the second that due to the ends of the sleeve, at which the flow does not immediately take advantage of the increase of section.

It is evident from (6) that the presence of a sleeve on the rod causes a decrease in the thermal gradient along the rod. The difference in temperature between a rod with a sleeve and a free rod, at points corresponding to the middle of the sleeve, will be from (4)

$$\frac{H_0}{qk}b - \frac{H_0}{qk + q'k'}\left\{b + \frac{q'k'}{qk}\frac{1}{\alpha}\tanh \alpha b\right\}.$$

Taking the poorest conductor investigated, platinoid (mean $k = 0{\cdot}10$), for which the mean heat flow was 0·34 cal. per second, this difference amounts to 0·34° C.

For all the other conductors the difference is considerably smaller.

Now the temperatures at the two points of the guard tube at the same heights as the centres of the two sleeves on the rod are made to agree as closely as possible with those at the centres of the sleeves. Hence, assuming a linear temperature variation along the guard tube, the maximum temperature difference between the rod and guard tube on account of the sleeves, which would occur at the ends of the sleeves, would be, in the case of platinoid, the poorest conductor, 0·34° C. The experimental agreement of temperatures was to within 1° C., hence the correction to be made on account of the thermocouple sleeves may therefore be made by using the length of free rod equivalent to the portion of rod enclosed by sleeve. We have, then, for the corrected values of the distances of the two thermocouples on the rod from the lower end of the rod, that is, x_A, x_B of equation (1)

$$x_A = a_1 + b'$$
$$x_B = a_1 + a_2 + 3b',$$

where a_1 is the distance from the lower end of the rod to the near edge of the first sleeve, and a_2 the distance between the near edges of the first and second sleeves.

Correction for the Heat Loss along the Thermocouple Wires.

On account of the finite cross-sectional area of the thermocouple wires, some of the heat flowing down the rod was diverted into the thermocouple wires. The correction was taken as the heat lost down the two wires of the upper thermocouple, the thermal gradient down the wires being taken as equal to that down the rod. This over-estimates the correction, since the thermocouple wires start out horizontally from the sleeve.

Let k_L, q_L, k_L', q_L' be the respective thermal conductivities and areas of cross section of the wires. Then the heat flow down one wire is

$$k_L q_L \frac{d\theta}{dx} = \frac{k_L q_L}{kq} H_0 \text{ cals. per second.}$$

For the wires used we have the following constants: $q = 1 \cdot 2 \times 10^{-3}$ sq. cm., for chromel, $k_L = 0 \cdot 06$, for alumel $k'_L = 0 \cdot 13$, both conductivities being at the ordinary temperature. The variation of conductivity of the materials of the wires was neglected, as it was not likely to affect the values of k by as much as 0·5 per cent. We have then for the heat lost down the upper thermocouple wires per second

$$\frac{q_L H_0}{kq}(k_L + k'_L) = 0 \cdot 00096 \frac{H_0}{k}. \qquad (5)$$

For a good conductor ($k = 1 \cdot 0$), the correction amounts to 0·096 per cent. of H_0, and for the poorest conductor ($k = 0 \cdot 10$), to 0·96 per cent. of H_0. This must be subtracted from the heat flow down the rod.

Effect of the Thermal Expansion of the Rods.

At high temperatures the effect of thermal expansion of the rods must be taken into account.

Now

$$k = \frac{H_0}{(v_B - v_A)} \left\{ \frac{x_B - x_A}{q} \right\}_v, \qquad (6)$$

where $\left\{ \frac{x_B - x_A}{q} \right\}_v$ denotes the value of $\left\{ \frac{x_B - x_A}{q} \right\}$ at temperature V. Then if β is the coefficient of linear expansion of the material of the rod,

$$\left\{ \frac{x_B - x_A}{q} \right\}_v = \left\{ \frac{x_B - x_A}{q} \right\}_0 (1 - \beta v) \text{ approx.} \qquad (7)$$

Thus the value found for k must be multiplied by $(1 - \beta v)$ to give the corrected value. The correction amounts to about 1 per cent. for a rise of 500° C.

Correction for the Leads in the Power Circuit.

A correction must be made for the fact that the No. 36 nichrome wire was not wholly wound on the mica sleeve, but at each end a length of about 0·8 cm. was left to make contact with the copper leads supplying current to the heating coil. Hence a fraction of the potential difference measured was expended on the leads and the nichrome wire, not on the sleeve. Also the passage of the current through the nichrome wire raised its temperature above that of the wire on the sleeve and some of the heat generated in it would in consequence reach the sleeve by conduction along the wire.

(1) *Potential Drop in Leads and Nichrome.*—The nichrome leads were usually 1 cm. and 0·5 cm. long respectively, 0·02 cm. in diameter, hard soldered to the copper leads of 95 cm. of 0·068 cm. diameter wire at the temperature of the apparatus, and 15 cm. of the same wire at the room temperature. The resistance of the copper wire was taken as 6×10^{-4} ohm per centimetre cube, and its temperature coefficient of resistance 1/290. The resistance of the nichrome wire was found to be 0·380 ohm cm. cube, and its temperature coefficient 11×10^{-5}. Taking these values the resistance of the leads was found to be 0·63 ohm at 17° C. and 0·67 ohm at 400° C. A mean value of 0·65 ohm was taken for all temperatures, as a slight error in the value of the resistance produced an extremely small error in the value k. Hence for a current of A amperes and a potential difference of V volts across the heating coil, the true power expended on the sleeve is

$$A\{V - 0\cdot65A\} \text{ watts.} \tag{8}$$

(2) *Heat Conducted by the Nichrome Wires to the Sleeve.*—Let H_0 be the total heat generated in the nichrome, L the total length of the nichrome wire, v the temperature excess of any point of the nichrome lead over that of the sleeve, then with the usual notation the equation for the distribution of temperature excess v along the wire will be, in the steady state,

$$qk\frac{d^2v}{dx^2} + \frac{H_0}{L} - phv = 0. \tag{9}$$

The solution of this equation may be written

$$v = A \sinh \sqrt{\frac{ph}{qk}}\, x + B \cosh \sqrt{\frac{ph}{qh}}\, x + \frac{H_0}{Lpk}. \tag{10}$$

The correction may be worked out approximately by taking the temperature gradient down the copper leads as being the same as that down the rod, and the temperature at the nichrome copper junction as the same as that at the point where the nichrome joins the sleeve.

With these simplifications, and taking $x = 0$ at the middle point of the nichrome wire between rod and copper lead, l the total length of the nichrome lead,

$$v = 0 \quad \text{at} \quad x = l/2$$

$$v = 0 \quad \text{at} \quad x = -l/2.$$

Applying these, we have

$$A = 0,$$

$$B = -\frac{H_0}{Lph} \Big/ \cosh \sqrt{\frac{ph}{qk}}\frac{l}{2}.$$

Hence

$$v = -\frac{H_0}{Lph}\left[\frac{\cosh\sqrt{\frac{ph}{qk}}\,x}{\cosh\sqrt{\frac{ph}{qk}}\frac{l}{2}} - 1\right].$$

The heat flow into the sleeve from one wire is

$$-kq\left(\frac{dv}{dx}\right)_{(x = l/2)}$$

i.e.,

$$\frac{H_0}{L}\sqrt{\frac{qk}{ph}}\tanh\sqrt{\frac{ph}{qk}}\cdot\frac{l}{2}. \tag{11}$$

For the nichrome wires used, we have the following constants: $k = 0{\cdot}03$, $q = 3{\cdot}1 \times 10^{-4}$ sq. cm., $p = 0{\cdot}063$ cm., h (mean) $= 5 \times 10^{-4}$, $L = 38$ cm.

This gives for the flow of heat into the sleeve from the two wires a mean value of $0{\cdot}0167\ H_0$, where H_0 is the total heat generated in the nichrome. The corrected expression for the heat flowing down the rod from the sleeve is therefore

$$1{\cdot}0167\,(AV - 0{\cdot}65A)\left(1 - \frac{0{\cdot}00096}{k}\right).$$

Effect of Slight Differences in Temperature between the Rod and Guard Tube and of Slight Departures from Linearity of Temperature Distribution.

Four other effects have to be investigated :—

1. The effect of a slight temperature difference between corresponding points on the rod and guard tube, which involves the determination of the

coefficient of heat loss from the rod and its variation with temperature.

2. The departure of the temperature distribution from linearity in the heating coil portion of the rod.
3. The experimental investigation of the distribution of temperature along the guard tube.
4. The effect of the slight temperature difference between the wire constituting the heating coil and the rod surface at the same point.

1. Since the corrections were likely to be very small, approximate values of the coefficient of heat loss, h, were sufficient. A steady-state method was adopted, the heat input to the rod necessary to maintain a known temperature difference between the rod and guard tube being measured, when the rod was disconnected from the bottom disc. This determined the rate of loss of heat from the rod through the magnesia insulation.

The brass rod was suspended vertically along the axis of the guard tube, a heating coil being wound on it near its centre, and a thermocouple placed about 1·5 cm. below the heating coil.

A first series of experiments was made to test the law $H = h(v - v_0)S$ for a small range of temperature, so that h did not vary appreciably. The heat loss from the rod to the guard tube was found proportional to the difference of temperature between them.

To investigate the variation of h with temperature, experiments were made with the guard tube at various temperatures from about 80° C. to 400° C. The coefficient of heat loss, h, was found to vary in a linear manner from 0·00042 at 80° C. to 0·00060 at 395° C.

It was previously stated that the best possible agreement between the temperatures of the rod and the tube in the conductivity experiments was to about 1° C. We can now calculate the error introduced by this slight disagreement. Taking a temperature difference of 1° C. between all points of the rod and tube (in practice the difference will not be so large at all points) we find that for a poor conductor the heat loss amounts to 1·7 per cent. of the heat flowing down the rod, and for a good conductor, 0·32 per cent. This gives the maximum error likely to be made on this account.

2 and 3. There is a further small correction due to the fact that the heat does not enter the rod over an infinitely thin plane but over a finite length of the curved surface of the rod. For this reason the temperature distribution in the heating coil portion of the rod is not linear, and in this region the tempera-

tures at corresponding points of the rod and guard tube will not agree. It was calculated approximately by determining the distribution along the guard tube experimentally, and the distribution in the heating coil by approximate theory, and calculating the heat loss due to any temperate differences.

(1) *Temperature Distribution in the Heating Coil on the Rod.*—We can calculate the temperature distribution approximately by assuming the heat to be generated uniformly throughout the volume of rod covered by heating coil.

Let l_1, l_2 be the distances of the lower and upper ends of the heating coil from the bottom of the rod, H the heat generated per centimetre length of the heating coil.

Then in the part of the rod not heated, we have with the usual notation

$$qk\frac{d^2v}{dx^2} = 0$$

and therefore

$$v = \frac{\mathrm{H}}{qk}(l_2 - l_1)\,x$$

the temperature at the lower end of the rod being taken as zero.

In the part of the rod which is heated, we have

$$qk\frac{d^2v'}{dx^2} + \mathrm{H} = hp\,(v' - v_{\mathrm{T}}), \tag{14}$$

where v' indicates the temperature of the rod in the heated portion, and v_{T} the temperature of the guard tube at a corresponding point. The term on the right-hand side of (14) is very small and may be neglected.

Hence we have as the solution for v'

$$v' = -\frac{\mathrm{H}}{2qk}x^2 + \mathrm{A}x + \mathrm{B}.$$

The conditions to be satisfied are :—

$$v' = v \quad \text{at} \quad x = l_1$$

$$\frac{dv'}{dx} = 0 \quad \text{at} \quad x = l_2.$$

Applying these, we have

$$v' = \frac{\mathrm{H}}{2qk}(-x^2 + 2l_2x - l_1^2) \tag{15}$$

as the temperature distribution in the heating coil. The equation shows that the temperature does not increase in a linear manner in the heating coil, the temperature at any point being lower than if the gradient were linear.

(2) *Experimental Investigation of the Temperature Distribution along the*

Guard Tube.—The temperature of the guard tube was measured at four points with different heating currents for each coil, so that the distribution was found at different temperatures. The distribution was found to be very nearly linear from the lower end of the tube to the level of the lower end of the heating coil on the rod, beyond which the temperature remained very nearly constant.

(3) We have, therefore, the rod and guard tube agreeing in temperature up to the heating coil, beyond which the temperature of the rod increases according to the equation (15), and the temperature of the guard tube for the purpose of the correction may be taken as constant (see fig. 3).

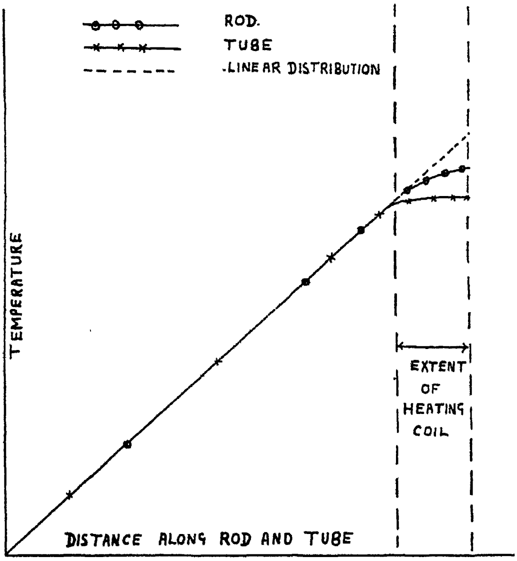

Fig. 3.—Diagram of Temperature Distribution in Rod and Tube.

We have,

$$\text{Heat lost from heating coil} = \int_{l_1}^{l_2} ph\,(v' - v_{\mathrm{T}})\,dx. \qquad (16)$$

We may take $v_{\mathrm{T}} = v'$ at $x = l_1$.

On substituting the value of v' from equation (15) and of v_{T}, and integrating, we have

$$\text{Heat lost} = \frac{ph}{3qk}\mathrm{H}_0\,(l_2^2 - 2l_1l_2 + l_1^2). \qquad (17)$$

Taking mean values this heat loss amounts to 0·19 per cent. H_0 for a good conductor ($k = 1{\cdot}0$) and 1·9 per cent. for a poor conductor ($k = 0{\cdot}10$), being negligible for a good conductor but appreciable for a poor conductor.

4. It has been assumed in the previous corrections that the temperatures at corresponding points on the heating coil and rod surface are equal. There is a further small heat loss due to the fact that the wire of the heating coil is hotter than the surface of the rod at a corresponding point.

This temperature difference may be calculated approximately from the equation

$$\frac{H_0}{(l_2 - l_1)} = \frac{pk''}{t''}(v'' - v), \tag{16}$$

where v'' is the temperature of the heating coil at any point. Since the temperature gradient along the guard tube is adjusted to equality with that along the rod, the heat lost from the coil will be

$$ph(v'' - v)(l_2 - l_1) = \frac{hH_0t''}{k''} = 0\cdot001H_0$$

for a mean value of h.

Thus the heat loss on this account does not exceed 0·1 per cent. H_0, and may therefore be neglected.

The final corrected expression for the heat flowing down the rod is therefore

$$A\{V - 0\cdot65\,A\}\{1\cdot0167\}\left\{1 - \frac{0\cdot00096}{k}\right\}\left\{1 - \frac{0\cdot0019}{k}\right\}$$

i.e.,

$$1\cdot0167\,A\{V - 0\cdot65\,A\}\left\{1 - \frac{0\cdot0019}{k}\right\}. \tag{17}$$

Calibration of the Thermocouples.

The method used for calibrating the couples is given on p. 60. Three different couples were tested at different times and after different heat treatment. The results show that the thermoelectric power of the combination is very constant. Results for different couples did not differ by more than one part in two thousand. The mean thermoelectric power was found to be 41·30 micro-volts per ° C.

Positions of Thermocouples on the Guard Tube.

The positions of the four thermocouples soldered to the outside of the guard tube were measured to 0·05 cm. with a low-power microscope.

Couple.	Distance above lower end of tube.
	cm.
1	0·10
2	1·80
3	5·65
4	8·05

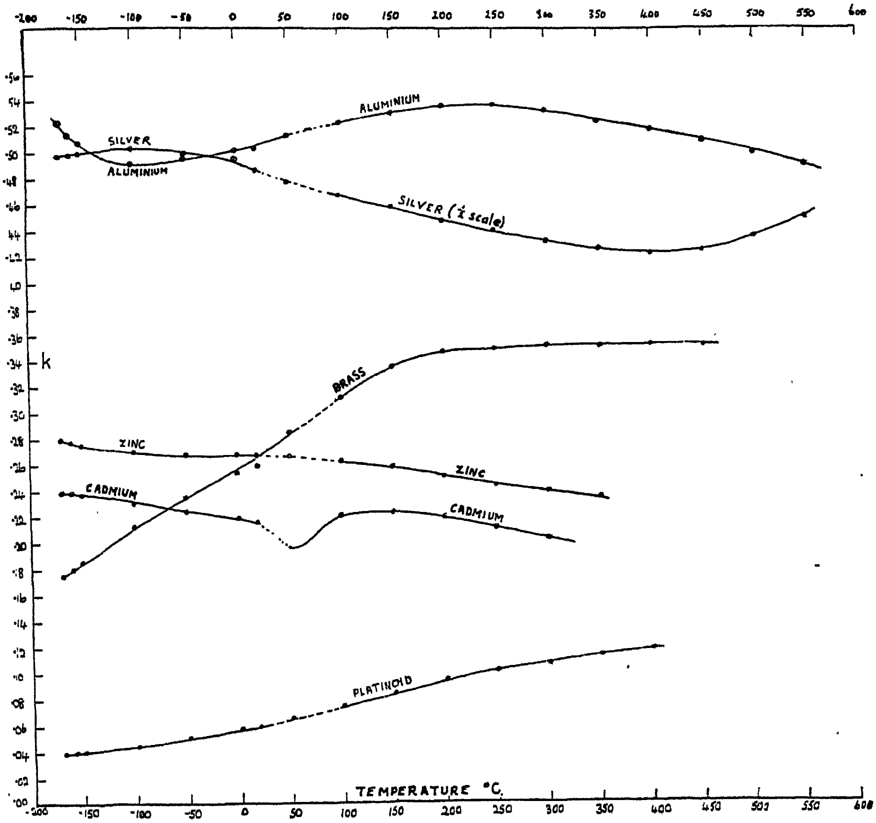

Fig. 4.—Variation of Thermal Conductivity with Temperature —170° to 18° C., results of Lees; 50° to 550°, results of present experiments.

Results of the Thermal Conductivity Measurements.

I. *Aluminium.* 0·99 Al. Density at 20° C. = 2·70.* $x_B - x_A = 3\cdot87$ cm.

The values of current and voltage given are the corrected values. The temperature differences are given in "ohms" on the potentiometer. One ohm corresponds to 2×10^{-4} volt or 4·87° C.

Current amp.	Voltage.	Temperature difference "ohms."	Mean temperature of rod.		Conductivity k.
			"Ohms."	° C.	
0·215	2·86	0·79	13·83	83	0·527
0·248	3·22	1·07	16·92	100	0·508
0·267	3·50	1·20	19·54	120	0·525
0·357	4·88	2·23	33·58	179	0·530
4·416	5·63	2·96	38·62	204	0·537
0·468	6·38	3·76	45·63	238	0·540
0·550	7·48	5·24	57·20	296	0·534
0·577	7·94	5·99	62·74	322	0·528
0·644	9·02	7·54	71·75	365	0·521
0·686	9·47	8·50	77·25	392	0·518
0·711	9·74	9·04	79·12	403	0·519
0·787	10·75	11·30	89·02	447	0·507
0·843	11·81	13·44	99·43	498	0·501
0·856	11·78	13·82	100·3	498	0·493
0·882	12·15	14·61	103·2	519	0·496
0·956	13·19	16·97	110·3	554	0·503

II. *Silver.* 0·999 Ag. Density at 21° C. = 10·47. $x_B - x_A = 3\cdot86$ cm.

Current amp.	Voltage.	Temperature difference "ohms."	Mean temperature of rod.		Conductivity k.
			"Ohms."	° C.	
0·321	5·75	1·42	29·60	164	0·896
0·429	7·59	2·52	44·02	235	0·887
0·464	8·21	3·03	50·11	265	0·864
0·513	9·15	3·68	56·68	297	0·878
0·512	9·15	3·80	62·61	326	0·881
0·563	10·44	4·83	75·45	387	0·838
0·611	11·47	5·70	82·58	422	0·846
0·674	12·25	6·66	89·87	459	0·853
0·726	13·34	7·63	95·28	486	0·872
0·779	14·14	8·70	102·5	521	0·867
0·867	15·28	10·12	111·7	565	0·897

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* Figures for purity and density taken from Lees, 'Phil. Trans.,' A, vol. 208 (1908).

III. *Zinc.* "Pure redistilled zinc." Fracture crystalline with crystals radiating from axis of rod. Density at 21° C. = 7·10. $x_B - x_A = 3 \cdot 83$ cm.

Current amp.	Voltage.	Temperature difference "ohms."	Mean temperature of rod.		Conductivity *k*.
			"Ohms."	° C.	
0·270	4·47	3·06	23·71	136	0·265
0·271	4·79	3·35	27·56	153	0·257
0·272	4·67	3·34	28·92	163	0·256
0·319	5·36	4·46	31·92	176	0·257
0·317	5·56	4·76	37·70	206	0·249
0·411	7·15	8·14	53·40	282	0·241
0·417	7·37	8·44	52·78	279	0·244
0·466	8·24	10·86	61·86	313	0·237
0·514	9·26	13·33	70·99	367	0·238

IV. *Cadmium.* "Pure redistilled cadmium." Density at 21° C. = 8·64. $x_B - x_A = 3 \cdot 86$ cm.

Current amp.	Voltage.	Temperature difference "ohms."	Mean temperature of rod.		Conductivity *k*.
			"Ohms."	° C.	
0·108	1·66	0·628	7·50	54	0·194
0·131	1·89	0·862	9·12	63	0·194
0·164	2·47	1·25	11·90	76	0·219
0·198	3·07	1·87	15·55	94	0·221
0·225	3·81	2·93	22·31	126	0·224
0·289	4·10	3·53	26·46	147	0·226
0·319	4·74	4·63	33·44	174	0·219
0·319	4·90	4·87	34·90	190	0·215
0·370	5·77	6·53	40·86	218	0·220
0·380	5·76	6·83	43·25	228	0·215
0·413	6·19	8·00	47·51	249	0·220
0·409	6·24	8·01	48·40	253	0·214
0·428	6·70	8·96	51·25	267	0·211

V. *Brass.* 0·70 Cu, 0·30 Zn (approx.). Density at 22° C. = 8·44. $x_B - x_A = 3 \cdot 78$ cm.

Current amp.	Voltage.	Temperature difference "ohms."	Mean temperature of rod.		Conductivity k.
			"Ohms."	° C.	
0·174	2·08	0·780	13·08	78	0·305
0·232	2·85	1·42	16·50	94	0·306
0·211	2·47	1·08	17·20	99	0·317
0·210	2·49	1·11	18·35	113	0·311
0·270	3·32	1·82	20·55	121	0·323
0·324	3·98	2·53	25·48	140	0·336
0·320	3·73	2·25	30·41	164	0·340
0·327	3·79	2·41	32·40	175	0·337
0·397	4·51	3·43	35·92	208	0·342
0·412	5·03	3·81	45·59	238	0·357
0·429	5·29	4·37	51·81	268	0·342
0·466	5·67	5·00	57·60	298	0·348
0·613	7·61	8·58	65·68	337	0·357
0·660	8·30	9·99	72·07	361	0·359
0·600	7·21	8·01	73·51	375	0·353
0·652	8·40	10·28	85·18	430	0·350

VI. *Platinoid.* Composition approximately that of German silver. Density at 22° C. = 8·66. $x_B - x_A = 3 \cdot 93$ cm.

Current amp.	Voltage.	Temperature difference "ohms."	Mean temperature of rod.		Conductivity k.
			"Ohms."	° C.	
0·191	3·32	4·93	27·89	159	0·0871
0·228	3·58	6·01	39·26	216	0·0915
0·286	4·71	8·70	40·72	227	0·104
0·272	4·55	7·67	44·47	240	0·109
0·297	4·78	8·84	57·78	305	0·108
0·321	5·32	10·76	60·62	318	0·107
0·343	5·45	11·18	69·13	360	0·113
0·380	6·04	13·27	80·39	415	0·117

Table of Thermal Conductivities of pure Metals and Alloys between — 170° and + 550° C. from the experiments of Lees and the present Experiments.

Substance.	Temperature ° C.																		Melting point.
	−170	−160	−150	−100	−50	0	+18	+50	+100	+150	+200	+250	+300	+350	+400	+450	+500	+550	
Aluminium	0·524	0·514	0·508	0·492	0·496	0·502	0·504	(0·514)	0·523	0·531	0·536	0·537	0·532	0·524	0·517	0·508	0·499	0·490	658
Silver	0·996	0·998	1·000	1·008	0·997	0·981	0·974	(0·956)	0·934	0·917	0·896	0·880	0·864	0·853	0·844	0·850	0·870	0·901	961
Zinc	0·280	0·278	0·276	0·271	0·268	0·269	0·268	(0·267)	0·264	0·259	0·252	0·245	0·240	0·237	—	—	—	—	419
Cadmium	0·240	0·239	0·238	0·231	0·225	0·219	0·217	0·196	0·222	0·224	0·220	0·212	(0·204)	—	—	—	—	—	321
Brass	0·175	0·181	0·186	0·213	0·235	0·254	0·260	(0·286)	0·314	0·337	0·348	0·352	0·354	0·354	0·355	0·354	—	—	—
Platinoid	0·039	0·040	0·041	0·045	0·051	0·058	0·060	0·066	0·075	0·085	0·094	0·102	0·108	0·114	0·118	—	—	—	—

Discussion of the Results.

In the case of pure metals the generally accepted rule, that the conductivity decreases with increase of temperature, does not appear to hold in all cases.

(i) *Aluminium.*—The conductivity appears to reach a maximum at 225° C., after which a decrease takes place to 550° C. The values are in good agreement with those given by Schofield* for a specimen of greater purity (99·7 per cent.) than that used in these experiments. They are, however, somewhat below the value 0·55 given by Griffiths† for the conductivity of a single aluminium crystal (99·7 per cent. purity) at 100° C.

(ii) *Silver.*—The conductivity is a minimum at about 400° C., after which a rise occurs to 575° C. No other values appear to have been given for silver at these temperatures.

(iii) *Zinc.*—The conductivity appears to decrease continually over a wide range of temperature from −170° C. to +370° C. The values agree with those given by Schofield for a specimen of 99·8 per cent. purity, but are about 18 per cent. below those given by Bidwell and Lewis‡ for single crystals of zinc. These results, and those for aluminium, support the view that the thermal conductivity of a metal increases as the purity of the specimen used increases.

(iv) *Cadmium.*—The results indicate that an abrupt fall and rise of conductivity takes place near 50° C., after which the normal steady decrease occurs. A transition point, reputed to occur at 64·9° C. may have some connection with the change, but further work is necessary to test this.

In the case of the two alloys tested, the rule that the conductivity increases with increasing temperature is confirmed, but the increase is not regular.

(v) *Brass.*—The conductivity of brass increases rapidly with temperature, an approximately linear law being followed to about 125° C., after which it tends to a constant value of 0·335 up to 450° C.

(vi) *Platinoid.*—A continuous increase of conductivity occurs with increase of temperature, an approximately linear law being followed.

Acknowledgment.

The work was carried out at East London College, under the direction of Professor C. H. Lees. I have to thank him for the loan of the rods, and for his kind interest and advice during the progress of the work.

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* F. H. Schofield, *loc. cit.*

† E. Griffiths, 'Proc. Roy. Soc.,' A, vol. 115, p. 236 (1927).

‡ C. C. Bidwell and E. J. Lewis, 'Phys. Rev.,' vol. 33, p. 249 (February, 1929).

The Thermal Conductivities of the Saturated Hydrocarbons in the Gaseous State.

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Introduction.

The purpose of the present research has been to investigate the bearing of molecular structure on the thermal conductivities of the gaseous saturated hydrocarbons. The first four members of this family of hydrocarbons, namely, methane, ethane, propane and butane, having conveniently low boiling points, were chosen as the subject of the research. In view of the results obtained for these gases, further experiments were carried out, using *n*-pentane and *n*-hexane.

The thermal conductivities of methane, ethane, *n*-pentane and *n*-hexane have been previously determined, and their values, together with the values obtained for the temperature coefficients and the names of the investigators, are shown below.

Gas.	Investigator.	Thermal conductivity in cals. cm.$^{-1}$ sec.$^{-1}$ °C.$^{-1}$.	Temperature.	Temperature coefficient.
			° C.	per °C.
Methane	Eucken	0·0000715	0	
	Zeigler	0·0000746	0	0·00655
	Winkelmann	0·0000647	7·5	
	Weber	0·0000720	0	
	Stefan	0·0000806	10	
Ethane	Eucken	0·0000426	0	
	Zeigler	0·0000496	0	0·00583
	Moser	0·0000431	0	
n-pentane	Moser	0·0000293	0	0·00580
n-hexane	Moser	0·0000260	0	0·00480

In the case of propane and butane, however, no previous values have been obtained. Thus, having regard to the variation in the results for methane and ethane, it is highly desirable, in order to check the accuracy of the results, that an experiment be carried out using some standard gas, the thermal conductivity of which is known. A determination therefore was made of the conductivity of air, the gas with which nearly every investigation of thermal conductivity has been concerned.

The method adopted in the present research is that known as the "hot-wire" method, the theory of which is given by Gregory and Archer in their paper on the thermal conductivities of air and hydrogen.*

In this method a wire, which is heated electrically, is stretched along the axis of a cylindrical glass tube maintained at a constant temperature. A compensating tube of shorter length in gaseous connection with the main tube is used to eliminate end effects.

Theory of the Method.

The theory relevant to the present system of tubes is that applicable to a length of wire l, given by the difference in length of the wires in the two tubes, at a uniform temperature of θ_1° C. stretched along the axis of a glass cylinder containing the gas.

For small ranges of temperature it may be assumed that the thermal conductivity varies linearly with temperature, *i.e.*,

$$K_\theta = K_0 (1 + \alpha\theta),$$

where K_θ and K_0 are the thermal conductivities at θ° C. and 0° C. respectively and α is the temperature coefficient.

On substituting in Fourier's law, we have that Q, the heat conducted across an elementary annulus of gas of radius r, length l, and thickness dr through a difference of temperature $d\theta$, is given by

$$Q = -2\pi r l K_0 (1 + \alpha\theta) \frac{d\theta}{dr},$$

whence on integration and substitution of the limits we have that

$$\frac{Q \log_e (r_2/r_1)}{2\pi l (\theta_1 - \theta_2)} = K_0 [1 + \tfrac{1}{2}\alpha (\theta_1 + \theta_2)] = K,$$

where r_2 and θ_2 are the radius and temperature of the inner surface of the tube and r_1 the radius of the wire.

Hence the quantity $Q \log_e (r_2/r_1)/2\pi l (\theta_1 - \theta_2)$, which may be determined by experiment, is the thermal conductivity of the gas K at a mean temperature of $\frac{1}{2} (\theta_1 + \theta_2)$.

The assumption that $K_\theta = K_0 (1 + \alpha\theta)$ has been verified at least over the range of temperatures considered in the present research by the experimental data obtained, it being found that on plotting K against $\frac{1}{2}(\theta_1 + \theta_2)$ a straight line was in every case obtained, the intercept of which with the conductivity axis gave K_0, which together with the slope of the line gives the temperature coefficient.

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* 'Proc. Roy. Soc.,' A, vol. 110, p. 91 (1926).

If C is the current flowing through the wires, R the resistance of the effective length l of the wires and J the mechanical equivalent of heat, then Q the heat conducted across the tubes for a difference of temperature $(\theta_1 - \theta_2)^\circ$ C. is equal to $C^2R/J - \phi$, where ϕ is the radiation heat loss at a temperature difference of $(\theta_1 - \theta_2)^\circ$ C., the values of ϕ being taken from the results obtained by Gregory and Archer (*loc. cit.*) for bright platinum wire.

The value of θ_2 is determined by using the equation for the conduction of heat through the glass tube, namely.

$$\frac{C^2R}{J} = \frac{2\pi k l \theta_2}{\log_e (r_3/r_2)}.$$

The external temperature of the glass tube being at 0° C., k is the thermal conductivity of pyrex glass and r_3 is the external radius of the glass tube. The value of k was found by a separate experiment to be 0·0016 cals. cm.^{-1} sec.^{-1} deg. C.^{-1}.

The Apparatus.

The tubes used in the research were of pyrex glass. They were constructed from a carefully calibrated piece of pyrex tubing, the internal radius of which was found by weighing the quantity of mercury required to fill a known length of the tube; the external radius being determined by taking a large number of readings with a micrometer screw.

The wire used to stretch along the axes of the tubes was of platinum. Its radius was found by weighing a length of 100 cm. in an assay balance. Two lengths of 24·32 cm. and 5·02 cm. of the wire, giving a difference of 19·30 cm., were then soldered to thick platinum leads and springs, using a gold solder.

The tubes, a manometer and a charcoal pocket, all of pyrex, were then fused together and the whole mounted on a board, the tubes themselves being rigidly fixed to a vertical brass mounting fitting into one arm of the U-tube of a galvanised iron ice bath, as shown in fig. 1. By means of the motor-driven paddle-wheel in the other arm of the U-tube a copious stream of ice-cooled water is forced through the U-tube, maintaining the external surface of the experimental tubes at a constant temperature of 0° C.

The electrical arrangement of the experimental system is shown in fig. 2. The long tube and the compensating tube are inserted in the two arms of a

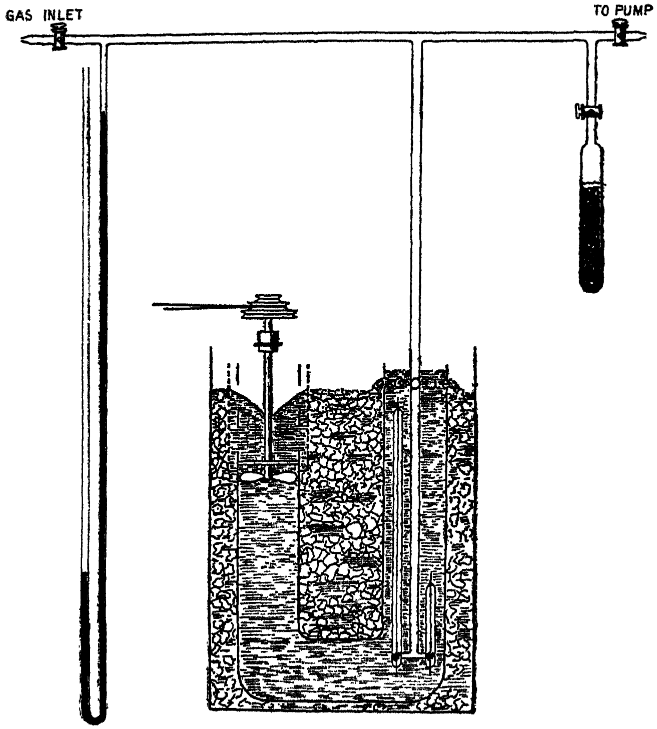
GAS INLET
TO PUMP

Fig. 1.

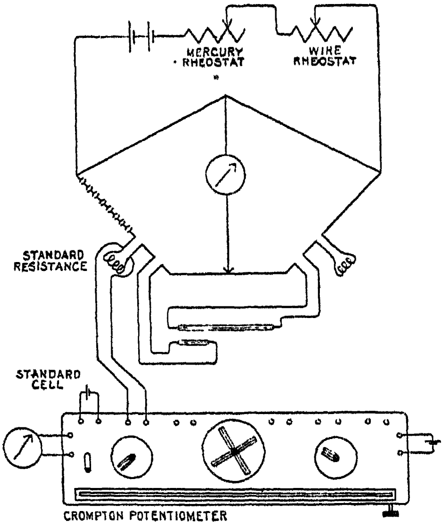
MERCURY RHEOSTAT
WIRE RHEOSTAT
STANDARD RESISTANCE
STANDARD CELL
CROMPTON POTENTIOMETER

Fig. 2.

Callendar and Griffiths bridge, the current through which can be varied by means of a system of rheostats. The leads from the tubes to the bridge are of heavily insulated copper wire and are all of equal length, being bound together so as to compensate for temperature variation along their length.

The current flowing through the wires of the experimental tubes for any setting of the bridge was determined by measuring the potential drop across a standard resistance of 1 ohm by means of a Crompton potentiometer. A compensating resistance of 1 ohm is inserted in the opposite side of the bridge so that the mid-point of the bridge may not be shifted by too large an amount.

In the earlier experiments the final adjustment of the current was made by means of a rheostat consisting of two stretched wires and a sliding screw contact. It was found, however, that on unscrewing the contact in order to move it a short distance, the resistance increased and the current through the tubes decreased with the result that the balance of the bridge, which is very sensitive to small variations of resistance, was momentarily upset. To obviate this and to reduce to a minimum the time required for a balance, a mercury rheostat was designed.

Two V-shaped parallel grooves in a piece of wood are filled to any required depth with mercury. The mercury troughs are connected electrically by means of a copper wire sliding along a brass rod. Thus the final adjustment of the current may be made without any break in the continuity. By means of this device the time taken for a set of readings was reduced to about one-third of that taken when the sliding screw contact was used.

In the case of the experiments carried out on *n*-pentane and *n*-hexane, owing to their relatively high boiling points (*n*-pentane boils at 36° C. and *n*-hexane at 69° C. under normal pressure) it became necessary to modify the constant temperature bath. Experiments were first carried out using the ice bath and working at low pressure. In the case of hexane, however, the maximum pressure was only 4 cm. of mercury, and hence observations could be obtained only in a region where the conductivity is rapidly falling off with pressure. A series of readings at constant pressure was taken, but the value of K_0 was, as would be expected, low.

Having conducted these experiments at 0° C. it was apparent that observations would have to be carried out at a higher pressure, and therefore it would be necessary to use a bath giving a steady temperature considerably higher than 0° C. Considerable difficulty was experienced in obtaining a satisfactory bath owing to the bridge, for the high currents used, being sensitive to a change of temperature as small as 0·001° C. Eventually, however, a bath was obtained giving reasonably steady temperatures in the neighbourhood of 50° C. This bath was ultimately used at room temperature for pentane, observations on which gas were carried out consecutive to those on hexane.

The bath consisted of a vacuum vessel, 40 cm. long and 10 cm. internal diameter, containing water in which the tubes were supported. A stirrer, consisting of a brass tube containing a rotating vane was supported in the flask by the side of the tubes. At the bottom of the stirring tube was supported a nichrome heating coil wound on mica, past which the water was driven by means of the rotating vane. The current in the heating coil was adjusted and the water stirred until an equilibrium temperature was reached, at which temperature the heat lost by evaporation at the surface of the water was compensated by the heat generated in the coil. A steady temperature was then obtained, which temperature was determined by means of a platinum thermometer using a second Callendar and Griffiths bridge.

By this means it was possible to obtain, without saturation, a pressure of about 10 cm. of mercury at a temperature of about 50° C. for hexane and a pressure of about 16 cm. of mercury at room temperature with pentane.

At 50° C., however, it was found that the hexane appeared to be dissolved in the mercury of the manometer which was still at room temperature. Moreover, on evacuating the apparatus this hexane was violently expelled from the mercury. This trouble was remedied, however, by enclosing the manometer in a steam jacket consisting of a glass tube through which the mercury levels could be observed.

Experimental Procedure.

The value of θ_1, the temperature of the wire, is determined by using the two tubes as a platinum thermometer. Thus it is necessary to know the fundamental interval of the tubes. To determine this, the effective resistance, *i.e.*, the difference in resistance, of the wires in the two tubes was found at 0° C., and at the temperature of steam, the tubes in the latter case being inserted into a specially constructed hypsometer. The resistances at the ice and steam points were determined, not by using an indefinitely small current, but by treating the experiment as a conductivity experiment and taking several values of the current, which could be determined by means of the potentiometer. Then on plotting C^2R against the resistance the true ice-point or steam-point could be determined by drawing a straight line through the points and extrapolating to zero wattage.

Then if R is the effective resistance at a temperature θ, we have that

$$\theta = \frac{R - R_0}{R_{100} - R_0} \times 100^\circ \text{ pt.},\ .$$

where R_{100} and R_0 are the effective resistances at 100° C. and 0° C. respectively.

With air in the tubes $(R_{100} - R_0)/100$ was found to be equal to 0·009185, 0·009190 and 0·009189 ohm per degree on the platinum scale. This gives a mean value of 0·009188 ohm per degree platinum. Actually the change in the value of the conductivity in taking the two extreme values of the fundamental interval is only one-twentieth of 1 per cent. It was found during the course of the experiments that the value of R_0 changed from time to time by small amounts, the change seeming to depend very largely on the gas in the tubes at the time of observation. It is, however, unnecessary to redetermine the fundamental interval since, although for a small change in R_0 the percentage change in $R - R_0$ for low values of θ may be appreciable, the percentage in $R_{100} - R_0$ is negligible. A determination, therefore, of the ice-point was made previous to each set of observations of the conductivity.

The values of θ are found first of all on the platinum scale of temperature and are then corrected to the centigrade scale. Having chosen a suitable value of θ_1, the bridge was set to the corresponding calculated value of R and the current through the bridge and the tubes was then adjusted by means of the rheostats until the bridge was balanced. The value of the balancing current was then determined by means of the Crompton potentiometer. This was repeated for a number of different pressures using the same bridge setting and hence the conductivity at a mean temperature between the wire and the inside of the wall was determined at a number of different pressures. This was repeated for a number of bridge settings, corresponding to different values of θ_1.

Correction for the Convective Heat Loss.

Maxwell's law states that the thermal conductivity of a gas should be independent of pressure. We have found, however, a slight increase of apparent conductivity with pressure over the range considered. This increase occurs even in that range of comparatively high pressures where the accommodation effect, determined by the ratio of the mean free path to the radius of the hot wire, may be taken as negligible; it is accordingly attributed to convection. Since the convective heat loss depends on the mass of gas present it must be a function of the pressure and therefore, if K_c is the true value of the conductivity and K is the apparent value of the conductivity as determined from the observations of current and resistance, we have that

$$K = K_c + f(P),$$

where $f(P)$ is a function of pressure.

In every case we have found that the increase of K with the pressure P is linear over the range from about 20 cm. of mercury upwards. Therefore, since K_c is independent of P we have assumed, for the purpose of making a small experimental correction for the convective heat loss, that $f(P)$ is a linear function of P, and thus by rectilinear extrapolation to $P = 0$, using all the values above 20 cm. of mercury, the true value K_c of the conductivity has been estimated.

With regard to the operation of accommodation no precise calculation can be made with the data available, but an approximate estimate for air shows that the ratio of the mean free path to the radius of the hot wire being of the order of 1/100 at a pressure of 20 cm. of mercury, accommodation involves a correction of about 0·2 per cent., which represents the resultant order of accuracy claimed in these experiments. At lower pressures this correction is, although not precisely known, certainly larger. Consequently it has not been considered safe to use such points in the process of extrapolation indicated above.

The result of plotting K against P in the case of air for three temperature gradients is shown in fig. 3 while the full results are embodied in the tables and the curves shown in fig. 5.

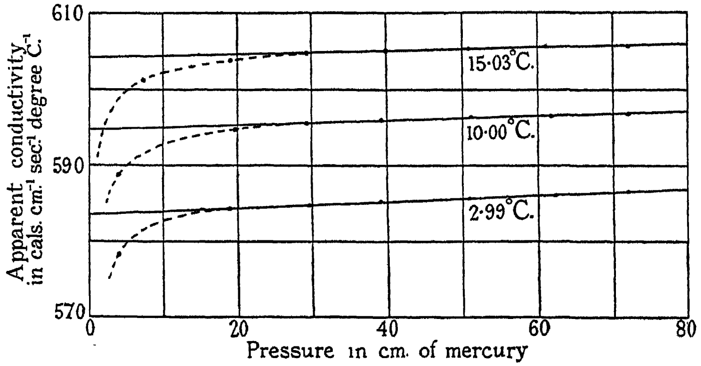

FIG. 3.

(Attention is drawn to the large scale of this diagram. Actually the points on the 10·00° C. and the 15·03° C. gradient in the neighbourhood of a pressure of 20 cm. of mercury are lower than the linear relation by only 0·1 per cent.)

Preparation of the Hydrocarbons.

The method adopted for the preparation of the gaseous hydrocarbons, was to reduce the appropriate iodide with nascent hydrogen, according to the equation

$$C_nH_{2n+1}I + 2H \longrightarrow C_nH_{2n+2} + HI,$$

the hydrogen being produced by the action of water on a zinc-copper couple.

The couple was prepared by passing hydrogen over a mixture of zinc dust and copper oxide in equal molecular proportions, heated electrically in a long tube to a temperature of 200° C. until no further water collected at the outlet.

The apparatus used in the preparation of the hydrocarbon gases is shown in fig. 4. The couple, contained in a litre flask, was moistened with distilled water and the appropriate alcohol. The corresponding iodide was now introduced into the flask, a few drops at a time, by means of a dropping funnel. In the case of methane the reaction set in immediately, but with ethane, propane, and butane it was necessary to warm the flask to start the reaction.

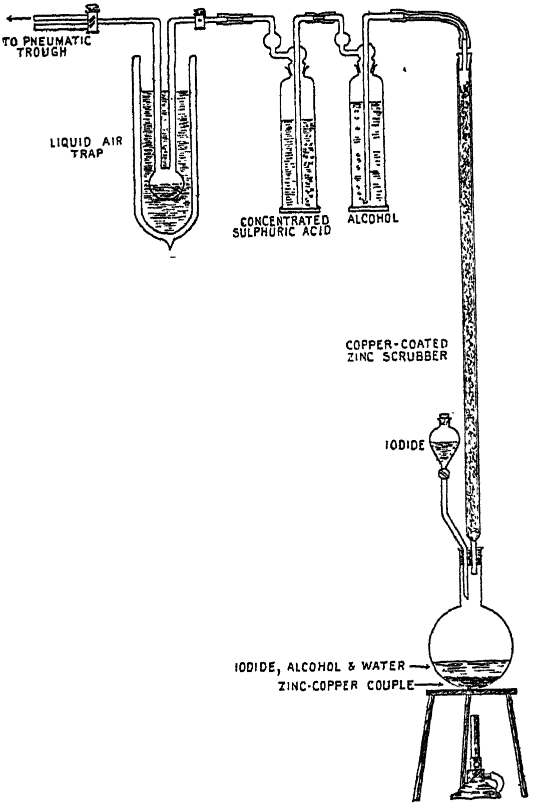

Fig. 4.

The liberated hydrocarbon then ascended through a scrubber containing granulated zinc coated with copper, to remove all traces of the iodide. The scrubber was prepared by allowing the zinc to act on an aqueous solution of copper sulphate until the latter had been decolorised.

The gas was now passed through bubblers containing the corresponding alcohol and concentrated sulphuric acid to remove any trace of alcohol or water which might be carried over. The sulphuric acid also served as an indicator to show whether any undecomposed iodide was still present, as the latter acting on the acid would produce a brown coloration.

After passing through the bubblers the gas was collected in a pneumatic trough, consisting of a 2-litre separating funnel inverted over water, the top of the separating funnel being connected through a wash bottle containing concentrated sulphuric acid and a phosphorus pentoxide tube to the gas inlet of the main apparatus.

To fill the tubes with the gas under investigation the apparatus was evacuated up to the tap of the separating funnel and the gas was then allowed to bubble through the sulphuric acid into the tubes. The tubes were then repeatedly evacuated up to the tap of the gas inlet and the gas flushed through until the bridge remained balanced for three consecutive evacuations. In the case of *n*-pentane and *n*-hexane the liquids were contained in a bulb connected directly to the main apparatus. The liquids were frozen by immersing the bulb in liquid air and the whole apparatus evacuated.

With the first four hydrocarbons it was found that for different specimens of the same gas consistent readings could not be obtained. It was suspected that slight traces of hydrogen and other hydrocarbons might be coming over with the gas. A liquid air trap was therefore inserted, as is shown in fig. 4, and the gas condensed. When a sufficient quantity of the gas had been collected the tap between the liquid air trap and the bubblers was closed and the gas was distilled over into the pneumatic trough, the first and last fractions being rejected. By this method two specimens of the gas were obtained which gave results in very close agreement, *i.e.*, for a given resistance an agreement of about 0·05 per cent. was obtained in the current readings.

In the case of methane, which boils at —164° C., it was necessary to have the liquid air boiling under reduced pressure in order to obtain a temperature low enough to condense the gas.

The preparation of the liquids *n*-pentane and *n*-hexane was carried out by Dr. F. L. Warren, the former by the action of a zinc-copper couple on *n*-amyl alcohol and the latter by means of the Wurtz reaction. The alcohols and iodides used in the preparation of the hydrocarbons were carefully purified by repeated fractionation, and the following are the boiling points of the specimens used.

Methyl alcohol—64·8° to 64·9° C. at 765·0 mm.
Methyl iodide—43·0° C. at 785·0 mm.
Ethyl alcohol—78·2° C. at 756·0 mm.
Ethyl iodide—72·3° to 72·4° C. at 760·0 mm.
n-Propyl alcohol—96·0° C. at 755·0 mm.
n-Propyl iodide—101·2° to 102·8° C. at 760·0 mm.
n-Butyl alcohol—118·0 to 119·0° C. at 760·0 mm.
n-Butyl iodide—130·2° to 130·8° C. at 770·0 mm.
iso-Butyl iodide—119·0° to 120·0° C. at 760·0 mm.
n-Amyl alcohol—135·0° to 135·8° C. at 750·5 mm.
n-Amyl iodide—153·0° to 154·5° C. at 763·0 mm.
Pentane—35·8° to 36·0° C. at 760·0 mm.
Hexane—68·5° to 68·9° C. at 766·0 mm.

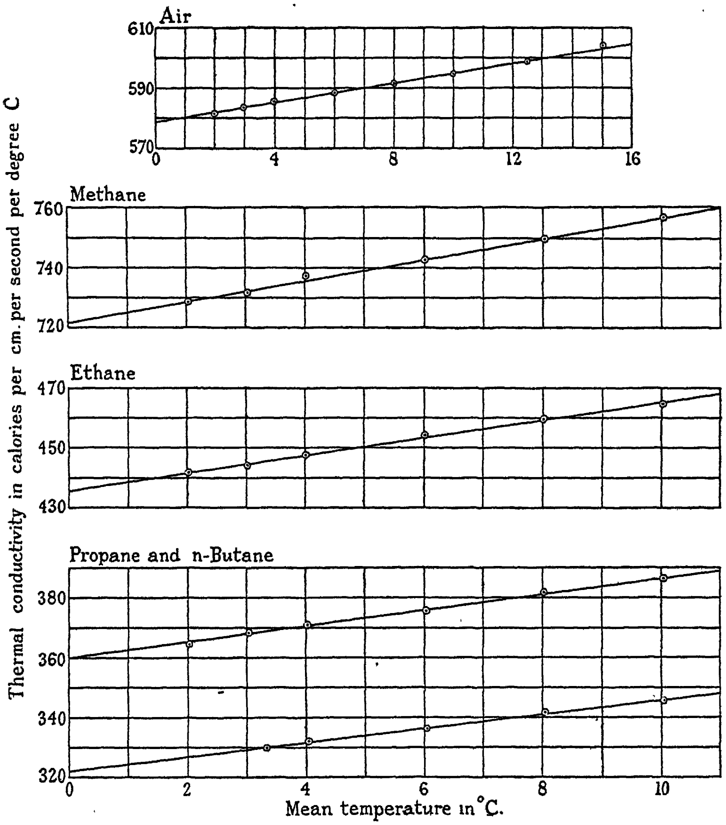

FIG. 5.

Results.

The following is a key to the symbols used in the tabulation of the results :—

P = pressure of gas in the tubes in centimetres of mercury.

ϕ = radiation heat loss from effective length of wire in calories per second.

θ_1 = temperature of wire in ° C.

θ_2 = temperature of inside of glass wall in ° C.

C = current in hot wire in ampères.

R = resistance of effective length of the wire at a temperature of θ_1° C., in ohms.

Q = heat loss from wire in calories per second corrected for radiation = $\frac{C^2R}{J} - \phi$.

J = mechanical equivalent of heat = 4·184 Joules per calorie.

l = effective length of hot wire = 19·30 cm.

r_1 = radius of hot wire = 0·005065 cm.

r_2 = internal radius of tubes = 0·4066 cm.

r_3 = external radius of tubes = 0·4663 cm.

k = conductivity of pyrex glass = 0·0016 cal. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$.

K = apparent conductivity of the gas at a mean temperature of $\frac{1}{2}(\theta_1+\theta_2)$° C. in cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$.

K_c = conductivity of the gas at a mean temperature $\frac{1}{2}(\theta_1+\theta_2)$° C. corrected for the convective heat loss.

K_0 = conductivity of the gas at 0° C.

α = temperature coefficient per degree C.

Constants.

In the determination of θ_2,

$$\frac{2\pi l}{\log_e(r_3/r_2)} \, . \, k \, . \, J = 5 \cdot 9275.$$

Also

$$\frac{2\pi l}{\log_e(r_2/r_1)} = 27 \cdot 652, \qquad \log_e(r_2/r_1) = 4 \cdot 3855.$$

Air.

θ_1.	P.	R.	C.	ϕ.	Q.	$\theta_1-\theta_2$.	$K \times 10^7$.	$K_c \times 10^7$.	$\frac{1}{2}(\theta_1+\theta_2)$.
3·981	71·93	2·4023	0·10580	0·0000120	0·0064150	3·976	583·50	581·5	1·99
	61·24		0·10580		0·0064150		583·50		
	50·06		0·10575		0·0064088		582·93		
	39·32		0·10575		0·0064088		582·93		
	29·55		0·10570		0·0064014		582·26		
	19·04		0·10565		0·0063952		581·69		
	3·98		0·10510		0·0063286		575·64		
5·978	72·02	2·4209	0·12950	0·0000189	0·0096844	5·971	586·56	583·5	2·99
	62·16		0·12945		0·0096768		586·10		
	50·84		0·12940		0·0096692		585·64		
	39·14		0·12935		0·0096621		585·21		
	29·53		0·12930		0·0096545		584·75		
	18·87		0·12925		0·0096463		584·29		
	4·07		0·12855		0·0095499		578·42		
7·966	72·10	2·4394	0·14910	0·000028	0·012933	7·957	587·83	585·3	3·99
	61·06		0·12910		0·012933		587·83		
	49·48		0·14905		0·012925		587·42		
	40·09		0·14900		0·012916		587·03		
	29·23		0·14890		0·012898		586·23		
	19·16		0·14885		0·012889		585·83		
	4·46		0·14815		0·012768		580·31		
11·967	72·37	2·4766	0·18185	0·000059	0·019516	11·953	590·46	588·3	5·99
	60·21		0·18180		0·019504		590·12		
	50·77		0·18175		0·019494		589·79		
	39·84		0·18170		0·019482		589·45		
	29·29		0·18165		0·019472		589·16		
	18·79		0·18155		0·019452		588·52		
	4·38		0·18075		0·019279		583·30		
15·973	71·97	2·5138	0·20915	0·000093	0·026188	15·954	593·64	591·6	8·00
	61·98		0·20910		0·026175		593·35		
	51·25		0·20905		0·026163		593·08		
	40·47		0·20900		0·026150		592·78		
	28·86		0·20890		0·026126		592·23		
	18·80		0·20875		0·026088	15·955	591·37		
	3·98		0·20780		0·025852		585·98		
19·971	72·01	2·5509	0·23280	0·000126	0·032915	19·948	596·73	594·8	10·00
	61·63		0·23275		0·032900		596·47		
	51·25		0·23275		0·032900		596·47		
	39·18		0·23265		0·032872		595·96		
	29·18		0·23255		0·032845		595·47		
	19·68		0·23240		0·032802		594·69		
	4·05		0·23120		0·032473		588·72		
24·991	71·46	2·5974	0·25910	0·000169	0·041507	24·962	601·36	589·8	12·51
	61·71		0·25905		0·041489		601·09		
	49·48		0·25895		0·041458		600·65		
	40·20		0·25890		0·041441		600·40		
	30·08		0·25880		0·p41409		599·93		
	19·05		0·25860		0·041346		599·02		
	3·91		0·25745		0·040976		588·72		
30·018	71·97	2·6439	0·28245	0·000212	0·050200	29·982	605·52	604·2	15·03
	61·17		0·28245		0·050200		605·52		
	50·85		0·28240		0·050181	29·983	605·27		
	39·97		0·28235		0·050164		605·06		
	29·24		0·28225		0·050127		604·61		
	19·16		0·28205		0·050058		603·78		
	7·38		0·28145		0·049843		601·19		

$K_0 = 0\cdot0000579$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$. $\alpha = 0\cdot0028$ per deg. C.

Methane.

θ_1.	P.	Q.	$\theta_1 - \theta_2$.	K × 10^7.	K_0 × 10^7.	$\frac{1}{2}(\theta_1 + \theta_2)$.
4·045	73·51	0·0081732	4·039	731·75	728·5	2·03
	60·71	0·0081664		731·17		
	50·31	0·0081598		730·58		
	40·62	0·0081529		729·96		
	32·49	0·0081529		729·96		
	19·72	0·0081363		729·64		
6·043	73·67	0·012275	6·034	735·72	731·8	3·03
	58·18	0·012264		734·97		
	48·79	0·012256		734·55		
	41·03	0·012247		734·01		
	30·13	0·012240		733·47		
	18·51	0·012221		732·47		
8·032	73·83	0·016417	8·020	740·34	737·4	4·02
	61·19	0·016407		739·83		
	49·20	0·016396		739·39		
	41·16	0·016387		738·94		
	32·90	0·016376		738·47		
	18·93	0·016357		737·62		
12·031	73·78	0·024780	12·013	746·00	742·8	6·02
	62·10	0·024760		745·44		
	51·02	0·024746		744·82		
	36·86	0·024724		744·13		
	29·82	0·024724		744·13		
	20·04	0·024708		743·67		
16·035	73·77	0·033327	16·011	752·96	749·8	8·03
	61·77	0·033312		752·61		
	52·20	0·033298		752·30		
	43·16	0·033272		751·71		
	28·88	0·033241		751·17		
	18·67	0·033200		750·33		
20·026	73·79	0·042012	19·996	759·84	756·8	10·03
	62·03	0·042005		759·28		
	50·49	0·041973		758·96		
	39·92	0·041932		758·40		
	28·77	0·041902		757·84		
	18·96	0·041868		757·23		

$K_0 = 0{\cdot}0000721$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$.
$\alpha = 0{\cdot}0049$ per deg. C.

Ethane.

θ_1.	P.	Q.	$\theta_1 - \theta_2$.	K × 10^7.	K_c × 10^7.	$\frac{1}{2}(\theta_1 + \theta_2)$.
4·034	72·75	0·0049653	4·031	445·39	441·7	2·02
	63·19	0·0049550		444·55		
	51·89	0·0049495		444·06		
	40·85	0·0049442		443·59		
	30·72	0·0049390		443·12		
	20·43	0·0049336		442·63		
6·032	72·75	0·0074741	6·027	448·49	444·0	3·02
	63·19	0·0074611		447·70		
	51·89	0·0074545		447·31		
	40·87	0·0074415		446·53		
	30·72	0·0074281		445·73		
	20·43	0·0074216		445·34		
8·019	73·55	0·0100159	8·012	452·11	447·8	4·01
	62·37	0·0100078		451·74		
	48·10	0·0099848		450·70		
	41·40	0·0099775		450·37		
	31·21	0·0099619		449·67		
	19·85	0·0099241		447·78		
12·020	73·17	0·015208	12·009	457·98	454·0	6·02
	61·23	0·015189		457·41		
	51·94	0·015169		456·83		
	41·77	0·015151		456·26		
	30·62	0·015130		455·63		
	20·23	0·015094		454·56		
16·026	73·17	0·020525	16·011	463·62	459·7	8·02
	62·86	0·020493		462·87		
	51·91	0·020470		462·36		
	40·54	0·020448		461·87		
	31·10	0·020425		461·36		
	20·05	0·020381		460·36		
20·026	73·29	0·025947	20·008	469·01	464·8	10·02
	62·50	0·025922		468·55		
	51·86	0·025872		467·65		
	40·60	0·025847		467·20		
	30·19	0·025809		466·51		
	19·96	0·025772		465·84		

$K_0 = 0·0000436$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C^{-1}.
$\alpha = 0·0066$ per deg. C.

Propane.

θ_1.	P.	Q.	$\theta_1 - \theta_2$.	K × 10^7.	K_c × 10^7.	$\frac{1}{2}(\theta_1 + \theta_2)$.
4·066	73·21	0·0041266	4·063	367·31	364·3	2·03
	62·11	0·0041218		366·88		
	54·06	0·0041169		366·45		
	40·55	0·0041120		366·01		
	30·53	0·0041070		365·57		
	22·16	0·0041023		365·15		
6·064	73·31	0·0062154	6·060	370·93	368·4	3·03
	62·83	0·0062094		370·57		
	53·80	0·0062034		370·21		
	41·31	0·0061974		369·85		
	31·98	0·0061914		369·50		
	18·55	0·0061854		369·14		
8·052	73·52	0·0083259	8·046	374·23	371·0	4·03
	62·56	0·0083121		373·61		
	52·15	0·0083052		373·30		
	41·69	0·0082983		372·99		
	28·89	0·0082840		372·35		
	19·46	0·0082772		372·04		
12·053	73·50	0·012619	12·044	378·91	375·5	6·03
	62·77	0·012602		378·42		
	51·10	0·012584		377·88		
	41·10	0·012567		377·36		
	30·22	0·012550		376·84		
	21·45	0·012541		376·58		
16·051	73·60	0·017057	16·039	384·59	381·8	8·03
	62·53	0·017036		384·12		
	49·45	0·017016		383·67		
	40·97	0·016995		383·21		
	31·66	0·016976		382·76		
	21·12	0·016966		382·54		
20·057	73·50	0·021595	20·042	389·67	386·4	10·04
	62·95	0·021560		389·04		
	52·43	0·021525		388·42		
	40·89	0·021503		388·01		
	29·44	0·021480		387·61		
	20·66	0·021468		387·39		

$K_0 = 0{\cdot}0000360$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$.
$\alpha = 0{\cdot}0074$ per deg. C.

n-Butane.

θ_1.	P.	Q.	$\theta_1 - \theta_2$.	K × 10^7.	K_c × 10^7.	$\frac{1}{2}(\theta_1 + \theta_2)$.
6·677	64·74	0·0061728	6·673	334·52	329·8	3·34
	52·39	0·0061607		333·98		
	40·52	0·0061428		332·92		
	29·97	0·0061310		332·28		
	20·99	0·0061130		331·30		
	10·36	0·0061000		330·60		
8·085	63·85	0·0075162	8·080	336·42	332·1	4·05
	50·08	0·0074964		335·53		
	41·19	0·0074832		334·94		
	30·83	0·0074633		334·05		
	19·24	0·0074501		333·46		
	8·67	0·0074302		332·57		
12·085	63·66	0·011377	12·077	340·69	336·6	6·05
	52·26	0·011353		339·97		
	40·44	0·011329		339·23		
	31·64	0·011312		338·74		
	21·17	0·011287		337·99		
	10·18	0·011256		337·05		
16·090	63·48	0·015385	16·079	346·03	341·5	8·05
	52·34	0·015345		345·14		
	41·66	0·015317		344·51		
	31·16	0·015288		343·86		
	20·80	0·015250		343·00		
	10·63	0·015211		342·13		
20·090	61·06	0·019464	20·076	350·61	345·8	10·05
	53·04	0·019419		349·82		
	42·09	0·019376		349·04		
	32·22	0·019332		348·25		
	20·93	0·019289		347·47		
	9·87	0·019235		346·50		

$K_0 = 0·0000322$ cals. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$.
$\alpha = 0·0074$ per deg. C.

In the above tabulated results the values of θ_1, the temperature of the wire, and $\theta_1 - \theta_2$, the actual temperature gradient through the gas, have been given to 0·001° C. in order to show the smallness of the correction for the drop of temperature through the glass wall of the tube. Actually these temperatures are correct only to 0·01° C. and accordingly the final value of the mean temperature is shown to this degree of accuracy. It should be realised, however, that while the actual temperature can be obtained correct only to 0·01° C. the sensitivity of the bridge system, with the relatively large currents employed, is such that a change of temperature of the order of 0·001° C. can be readily detected, and the control is such that the temperature can be maintained constant to this accuracy.

It will be seen therefore that since the calculation of the apparent conductivity K involves the temperature difference, the actual value of the apparent conductivity is, for low values of $\theta_1 - \theta_2$, only correct to three significant figures. In considering the variation of apparent conductivity with pressure at constant temperature, however, account may properly be taken of the fourth significant figure of the apparent conductivity K.

The temperature of the outside of the glass tubes has been assumed to be equal to that of the circulating water. Considering the values of Q obtained in the case of air and assuming the thermal conductivity of water to be 0·0013 c.g.s. units, it would be necessary to have a stationary surface film of water on the tubes 1·3 mm. thick to introduce an error of 0·25 per cent. in the value of $\theta_1 - \theta_2$. It was assumed that with the high rate of circulation used no stationary film approaching this thickness could exist. This view has since received confirmation by a direct experimental investigation, shortly to be published by Dr. H. Gregory, in which the actual temperature of the outside wall has been determined. Working with the same ice-bath under the same conditions of circulation, no change in the temperature of the outside wall so large as 0·01° C. could be detected when a temperature gradient was established between the wire and the wall of the tube.

Discussion of the Results.

On plotting the results for the thermal conductivities at 0° C. of the gases methane, ethane, propane and butane against their respective molecular weights it was found that a smooth curve could be drawn through the four points obtained. Moreover the curve, which is shown in fig. 6, was found to be hyperbolic, the relation between the thermal conductivity at 0° C. and the molecular weight ($O_2 = 32$) being best given by the equation

$$(K_0 - 0{\cdot}00002227)(M - 5{\cdot}53) = 0{\cdot}0005241,$$

where M is the molecular weight.

By substituting the appropriate molecular weights of pentane and hexane in the above relation the values of K_0 may be calculated, and the object of the further investigation into the thermal conductivities of these two hydrocarbons was to determine whether the relation obtained was valid for the higher members of the series. Reference to fig. 6, in which the above relation is plotted, and also to the summary of results, will show that the agreement between the calculated and the experimental values of K_0 for pentane and hexane is only fair. Owing, however, to the difficulties encountered, the accuracy of the values obtained for these two vapours cannot be compared with that of the first four gases. Observations were taken at one pressure and the values are only given as an indication that the relation obtained, connecting the conductivities at 0° C. of the first four saturated hydrocarbon gases with molecular weight, may hold for the higher normal members of the series.

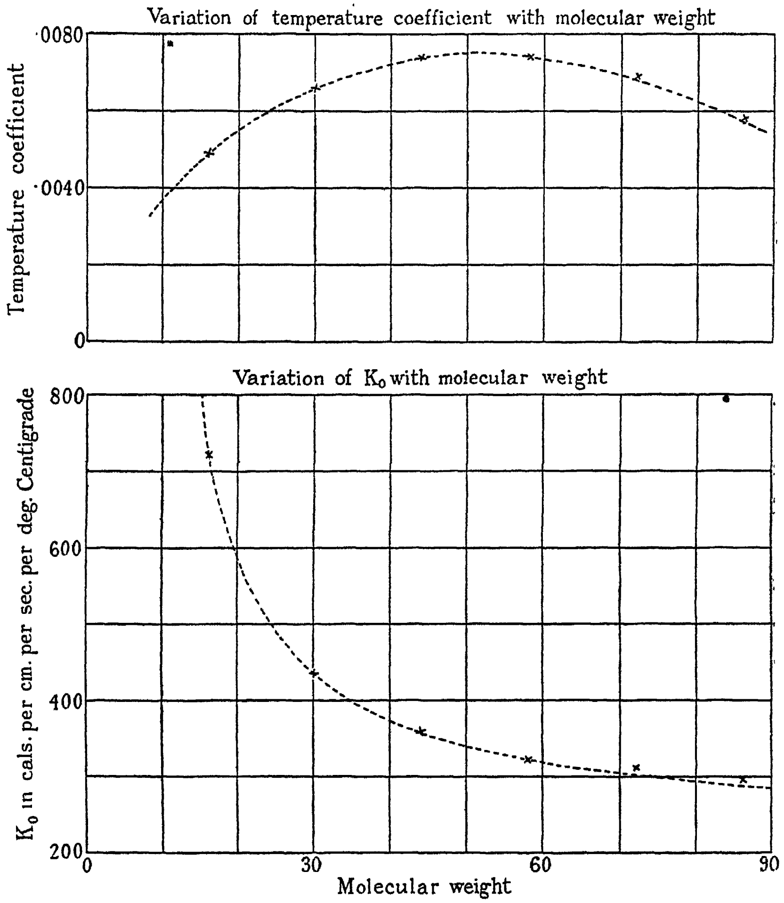

FIG. 6.

With reference to the temperature coefficients which are also plotted against the molecular weight in fig. 6 it will be noticed that an increase with molecular weight is observed for the first three hydrocarbons. The temperature coefficients of propane and normal butane are equal, after which a further increase in the molecular weight results in a decrease of the temperature coefficient.

A determination of the thermal conductivity of iso-butane was also made. The results, however, are not included in detail in view of the fact that sufficient iso-butyl iodide was available to prepare only one specimen of the gas. The liquid-air distillation method of preparation was, however, used, which method gave remarkably good agreement between every specimen of the first four gases prepared.

The following is a summary of the results obtained :—

Gas.	Molecular weight.	K_0 (calculated).	K_0 (experimental)	Temperature coefficient.
				per ° C.
Methane	16 04	0 0000721	0 0000721	0 0049
Ethane	30 06	0 0000436	0 0000436	0 0066
Propane	44 08	0 0000359	0 0000360	0 0074
n-Butane	58 10	0 0000322	0 0000322	0 0074
iso-Butane	58 10	—	0 0000332	0 0076
n-Pentane	72 12	0 0000303	0 0000312	0 0069
n-Hexane	86 14	0 0000288	0 0000296	0 0058
Air ...	—	—	0 0000579	0 0028

In conclusion, the authors wish to thank Professor G. P. Thomson for the facilities placed at their disposal and Dr. H. Gregory for his enthusiastic interest. The authors are especially grateful to Dr. F. L. Warren, of the Organic Chemistry Department of the Imperial College of Science, who prepared the iodides used in the preparation of the first four hydrocarbon gases and who also carried out the entire preparation of the specimens of the liquids pentane and hexane.

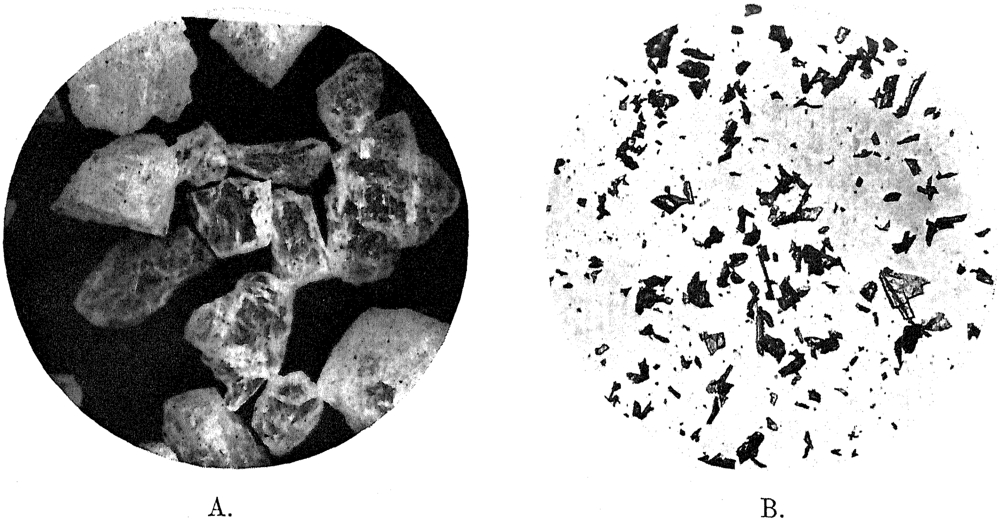
A. B.

FIG. 1.—Chabazite. A, ×8. B, ×60.

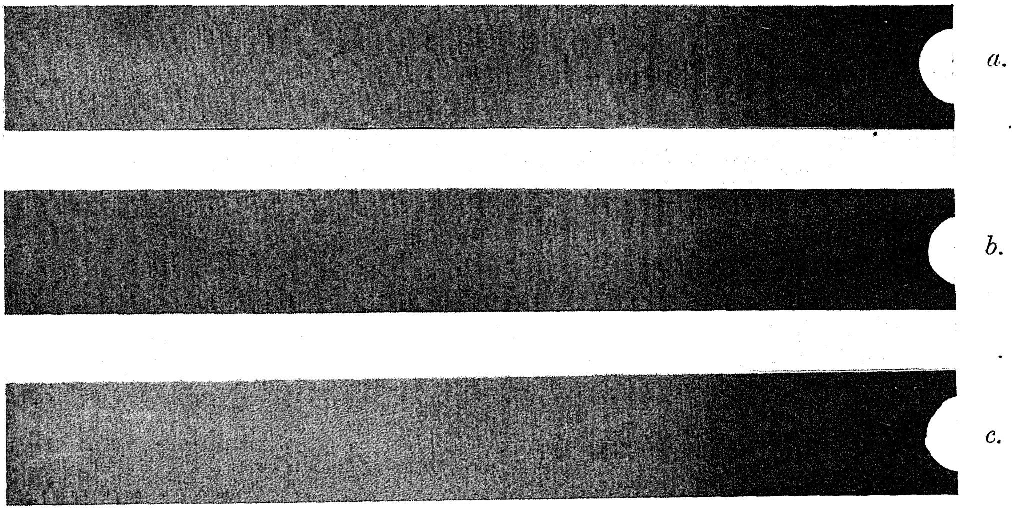

FIG. 3.—Powder Photographs: (*a*) Chabazite; (*b*) Dehydrated chabazite; (*c*) Chabazite after sorption of ammonia.

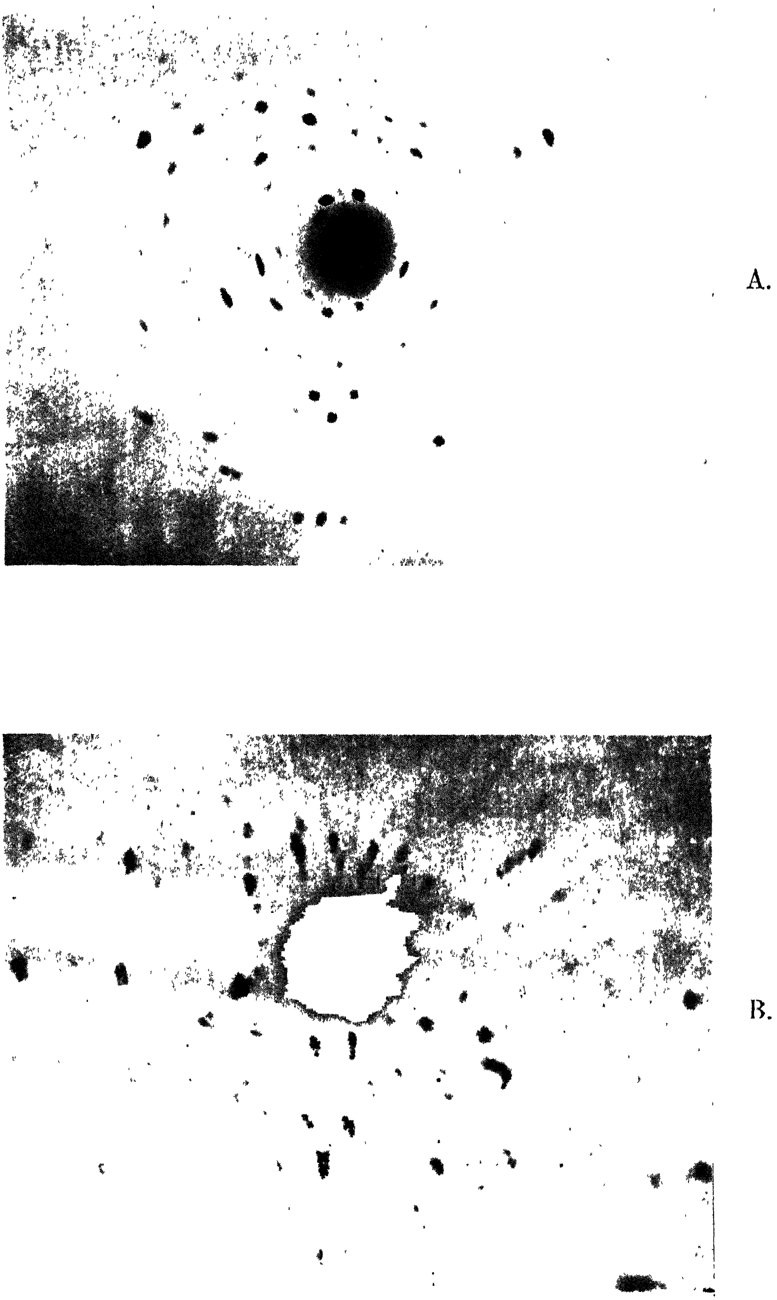

Fig. 2.—Chabazite, Laue figures.

The Sorption Process in the Zeolite Chabazite.

By Meredith Gwynne Evans.

(Communicated by A. Lapworth, F.R.S.—Received July 1, 1931.)

[Plates 1, 2.]

Introduction.

Seeliger* suggested that the sorption process in the case of chabazite might be due to the " spongy " nature of the sorbent and the entrance of the molecules of the gas into the molecular pores left by the dehydration of the crystal.

The rôle played by chabazite in the sorption process might be of special interest, since it is possible that similar processes may occur in many sorbents although not to so marked a degree.

Qualitative Evidence.

In another publication† the author has discussed the peculiar rate of sorption curve for ammonia on hydrated chabazite, and suggested that the peculiarity was due to the displacement of some water, from the hydrated chabazite, by the ammonia. The reverse process also occurs and water can displace ammonia from its sorbed state in dehydrated chabazite. It was found impossible to remove all the sorbed ammonia from dehydrated chabazite at 0° C. *in vacuo*, but if a little water was brought into contact with this " sorption complex " ammonia was freely evolved. It seems probable therefore, that the ammonia molecules might be occupying the vacant positions in the space lattice of chabazite, previously occupied by the water molecules.

Although on the removal of water from the chabazite the crystals remained intact, during the sorption of ammonia the crystals were broken up into a fine powder, which was still crystalline when examined microscopically.

Fig. 1 (Plate 1) shows the condition of dehydrated chabazite before and after a single addition of ammonia, whereas it was only after repeated dehydration and rehydration over a period of 6 months that the crystal powdered.

X-ray Analysis.

From a study of the positions and intensities of the reflections given by X-ray examination of chabazite at various stages of dehydration, Vegard and

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* Seeliger, ' Physik. Z.,' vol. 22, p. 563 (1921).

† ' J. Chem. Soc.,' vol. 214, p. 1,556 (1931).

Schjelderup* suggested that the water molecules played no important part in the actual structure of chabazite, and that the water could be removed without fundamentally altering the skeleton of the unit cell.

More recently analcite, a zeolite very similar to chabazite in properties, has been examined by Taylor† and its structure determined. Quoting from this paper: "The points occupied by the water molecules lie on non-intersecting trigonal axes of the cubic space group; no other atoms lie on these axes so that there are long channels passing through the structure wide enough to accommodate quite large atoms or molecules, and empty of everything but water molecules. There can be little doubt that these holes are in some way responsible for the ease with which the water may be removed from analcite and replaced by other materials."

The author has shown that ammonia was sorbed to some extent by hydrated chabazite, and during this process the crystals were not broken up as in the case of the dehydrated crystals. With a single crystal of hydrated chabazite mounted on an oscillating crystal table, an X-ray photograph was taken. Fig. 2, A (Plate 2) shows the result.

The crystal while still in position on the oscillating table was treated with ammonia at a pressure of about an atmosphere, and then a photograph was taken. Fig. 2, B (Plate 2) shows the X-ray photograph after sorption of ammonia by the single crystal. It is apparent that in photograph 2, B the same reflections occur and are in the same relation to each other, but all the reflections are blurred and elongated. The sorption of ammonia has brought about some very fundamental changes in the arrangement of the interior of the crystal. Although the reflections are too indistinct to render possible exact measurements or deductions as to the change in the parameter of the unit cell, it is possible to say that some straining or distortion has occurred in the interior of the crystal. The powder method of X-ray analysis particularly lends itself to this kind of work. All the work on chabazite for these photographs, such as dehydration and sorption of ammonia, was carried out with the powder in fine capillary tubes of boro silicate glass. The tubes were sealed *in situ* and mounted in the camera. Fig. 3, *a*, *b* and *c* (Plate 1) shows powder photographs of (*a*) chabazite, (*b*) dehydrated chabazite, (*c*) ammonia sorbed on dehydrated chabazite. It will be noticed that the photographs of chabazite (*a*) and dehydrated chabazite (*b*) are very similar, showing that no fundamental change in the structure of the crystal has occurred during the process of outgassing. After the sorption of ammonia, however, we find that the whole photograph (c) is much more indistinct, there being more fogging of the film, and the characteristic lines of chabazite are not so well marked.

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* Vegard and Schjelderup, 'Ann. Physik.,' vol. 54, p. 160 (1917).

† Taylor, W. H., 'Z. Krist.,' vol. 74, p. 1 (1930).

Evidence from the Heat of Sorption.

The next stage in the investigation was the measurement of the small amounts of heat evolved by the addition of very small quantities of ammonia to outgassed chabazite. Fig. 4 shows the apparatus used.*

The apparatus consisted essentially of a sorption bulb S, which could be connected as desired to the pumping system or to the " micro " gas burette (B) by means of tap T_1.

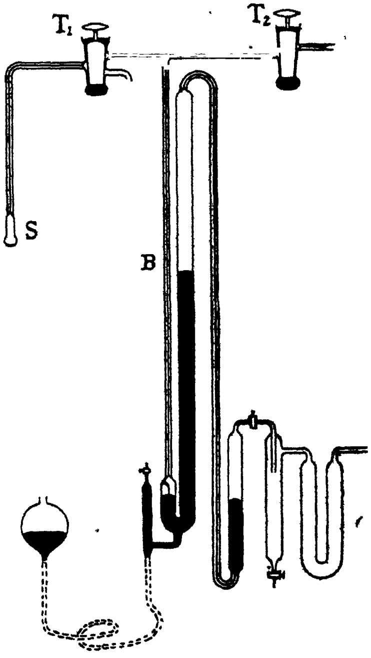

FIG. 4.

The short limb of the gas measuring system B contained a point to which the mercury was set, and the long limb was graduated in millimetres over a length of 800 mm.; the position of the point being known in terms of the scale on the long limb. The vacuum in the manometer head of the long limb could be renewed or checked from time to time by means of an arrangement first introduced by Young and worked in the same way as a Töpler pump. Tap T_2 connected the micro burette to the gas train. After outgassing the chabazite in the sorption bulb for 3 or 4 days at 350° C., small known amounts of ammonia were admitted by opening tap T_1. The sorption of the ammonia occurred practically instantaneously, and the heat effect was measured by means of the Bunsen ice calorimeter.

1. New, unused chabazite crystals were outgassed at 350° C., this being the only treatment they received. In this condition small amounts of ammonia were admitted, the heat being measured after each successive addition. After a total of 3 c.c. of gas had been admitted to the sorbent in this way, the calorimeter was removed and the crystals, which had fallen to powder during the sorption process, were outgassed at 350° C. for 3 days and the procedure

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* This apparatus was designed by Dr. M. Francis, of Manchester University.

repeated. The results plotted as h and dh/ds against S, where h is the heat in calories and S the sorption in cubic centimetres are shown in figs. 5, A and B.

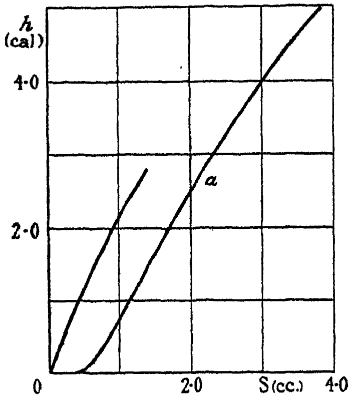

FIG. 5, A.

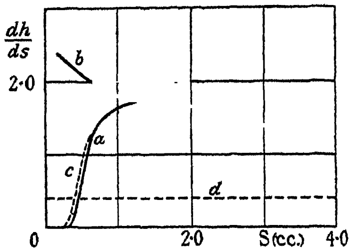

FIG. 5, B.

Curve *a* represents the measurements made with the new, unused chabazite. The values of dh/ds are initially small, but rapidly rise to a maximum and then slowly decrease with increasing values of the total sorption S. Curve *b* shows the values of dh/ds for the second process after the crystal has been shattered by the previous sorption. Here the initial values of dh/ds are great and gradually fall off with increase in the total sorption.

The broken curve *c* shows the results obtained when unused chabazite was powdered mechanically to approximately the same dimensions as chabazite shattered by the sorption process.

Theoretical Discussion.

It is probable that the outgassed chabazite presents to the gas phase holes vacated by the water molecules, which are now able to accommodate the sorbed ammonia molecules. Either because of a difference in the size of water and ammonia molecules, or because the entering ammonia molecules disturb the balance of forces in the crystal skeleton, the crystal is strained and finally shattered by the sorption of ammonia. The X-ray photograph, fig. 2, B, (Plate 2), shows a certain similarity to the distorted reflections obtained on examining a mechanically strained crystal.* In the latter case, naturally, the distortions are more marked.

This straining and final shattering of the crystal during the sorption process must involve the expenditure of a certain amount of energy, and therefore the measured heat of sorption in the early stages must be less than the actual heat of sorption, by an amount related to the work done in straining and finally shattering the crystal (fig. 5, curve *a*).

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* Czochralski, 'Z. Metallkunde,' vol. 15, p. 60 (1923).

From the X-ray powder photographs of the sorbent after sorption of ammonia (fig. 3, *c*) it appears that during the shattering of the crystal a certain amount of amorphous material is produced as indicated by the increased "fogging" of the film. Apart from the formation of amorphous material the shattering of the crystal will give rise to the formation of new crystal corners and edges possessing high surface energy.* Sorption will now take place preferentially on these new points of increased surface energy giving rise to a large heat of sorption, which will decrease as these active patches approach saturation.† When ammonia is removed from the chabazite in this state there is left a sorbent which will exhibit patches of high activity, and since the crystal has been permanently distorted by the previous sorption of ammonia, the subsequent processes will follow the normal course of sorption as suggested by Taylor,‡ and the value of dh/ds will fall gradually as the active patches become saturated.

This is considered to represent the state of affairs in the early stages of the process, but now the crystal is broken up and permanently distorted, and after the highly active patches have been saturated the sorbent will present a number of vacant places in the surface or in the bulk of the distorted crystals where ammonia molecules can be held. This seems to be a case similar to that postulated by Langmuir, but with the possibility of the sorbed molecules distributed in the crystal lattice as well as on the surface, and should be amenable to the same statistical treatment. It is considered that the conformity of the larger sorption measurements, over a range of pressure from 90 mm. to 600 mm. with the equation $S = abp/(1 + ap)$ offers some support to this idea. Moreover, there should be no difference in the energy change accompanying the sorption of a molecule in the later stages of sorption, since each molecule will occupy a similar position with reference to the surrounding crystal lattice, and one would expect to find a constant value of dh/ds over the range obeying the Langmuir isotherm. This was found to be the case. The broken line (*d*) in fig. 5 shows the constant value of dh/ds found in later stages of the sorption process (extrapolated into the range of fig. 5). To summarise the whole process :

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* See Rideal, "Surface Chemistry," p. 169–175.

† These patches of high activity may be considered to be both (*a*) imperfectly crystalline material (amorphous) produced in the shattering of the crystal, (*b*) and the edges and corners of the smaller crystals produced.

‡ H. S. Taylor, 'Z. Physik. Chem.,' vol. 125, p. 341 (1927).

(*a*) In the early stages of sorption the gas molecules penetrate the space lattice of the chabazite, the phenomenon being accentuated because of the exceedingly open nature of the lattice. This penetration of the lattice brings about straining and shattering of the crystal, and so reduces the measured heat of sorption. A similar process has been suggested by Rideal and Ward* to explain the low initial heats of adsorption found in the case of copper.

(*b*) The shattered crystal has now developed new corners and edges, and some amorphous material, and thus presents a number of patches of high activity, but when these are saturated sorption will occur at the definite places in the crystal lattice which were previously occupied by water molecules, and are now greatly exposed and highly accessible owing to the break up of the crystal.

It may well be the case that effects such as the protracted time required to approach equilibrium† in certain sorption processes may be due to changes such as are so manifest in the case of chabazite.

Summary.

(1) The changes in the zeolite chabazite during sorption have been investigated by means of X-ray examination of single crystals and of powders.

(2) The heats of sorption for very small additions of ammonia to the zeolite have been measured.

(3) A theory has been advanced to explain the results.

The author's best thanks are due to Professor Lapworth for his interest in this work and to Mr. J. B. M. Herbert, Dr. W. H. Taylor and Dr. A. J. Bradley for their help and advice. A grant from the Imperial Chemical Industries has helped to defray the expenses of apparatus.

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* Rideal, "An Introduction to Surface Chemistry," p. 235, and Rupp, 'Z. Electro-Chem.,' vol. 35, p. 586 (1929), catalytic action and penetration.

† Found in the case of glass and sodium chloride as sorbents. Mr. J. B. M. Herbert found no evidence of penetration of the sodium chloride from X-ray measurements.

The Interaction Energy of two α-Particles at Close Distances, determined from the Anomalous Scattering in Helium.

By H. M. Taylor, Clare College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received July 20, 1931.)

§ 1. In order to explain the fact that the scattering of high velocity α-particles by the lighter elements does not obey the Rutherford scattering law, it is necessary to assume that the inverse square law does not hold for the force between an α-particle and a nucleus when the distance between them becomes exceedingly small. There is evidence to show that the inverse square law does hold down to distances of about 10^{-12} cm., but that, as the distance is further reduced, the repulsive force changes to an attractive one, and it has been assumed by Gamow and others* that the potential energy of an α-particle in the field of a nucleus varies with the distance, as is shown in fig. 1 by the

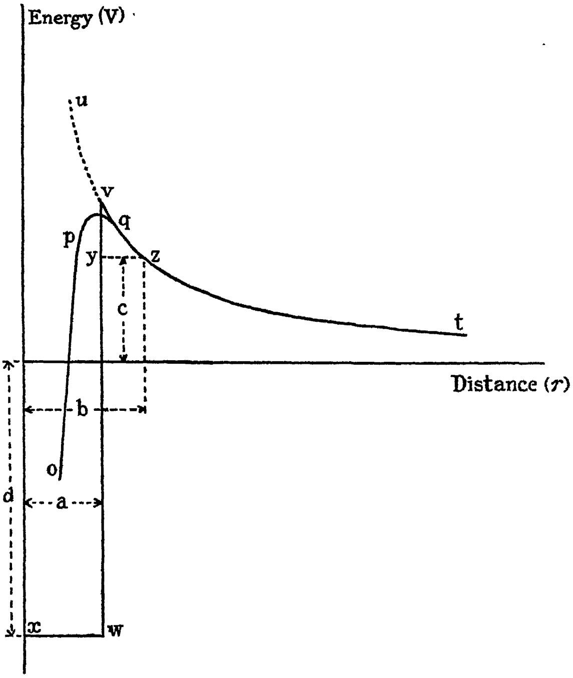

Fig. 1.

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* Gamow, ' Z. Physik,' vol. 51, p. 204 (1928) ; Gurney and Condon, ' Nature,' vol. 122, p. 439 (1928).

curve *t q p o*. The divergence from Coulomb's law, which is represented by the curve *t q v u*, does not become marked until a distance *a* is reached, but, for distances less than *a*, the force changes sign.

Sexl* has used a simplified form of such a potential field to calculate the decay periods of radioactive substances, and, in the present paper, an account is given of a method by which the anomalous scattering of α-particles by helium can be explained by assuming a potential field of the above type. In order to obtain a form for which the calculation is not unreasonably difficult, the field was simplified to the curve *t q v w x* of fig. 1. This field is defined by the two parameters *a* and *d*, and it is shown how the values of these parameters may be determined from the experimental results; the actual values obtained for the mutual potential energy of two α-particles are shown to scale in fig. 8. It is of interest to note that Sexl assumed the depth *d* of the "hole" to be zero in the case of the heavy elements, whereas it appears in this discussion that the depth is quite large in the case of helium (fig. 8), and that it is essential for the explanation of the experimental results to have the parameter *d* at our disposal.

It will be shown that it is possible to explain the experimentally observed deviations† of the scattering from classical Coulombian scattering, such as are shown in fig. 3, and that with a suitable choice of these two parameters *a* and *d* only, good agreement is obtained, not only for the variation of scattering with the velocity of the incident α-particles, but also for the variation with the two different angles of scattering shown.

It has unfortunately not been possible to make use of the experimental results for scattering at small angles, on account of the fact that the scattering is measured experimentally in a fairly wide belt of angles (8° to 12°, or 10° to 20°) and as the formulæ used contain the sine and cosecant of this angle, the uncertainty in these cases is too large, even if a mean value for the angle is suitably chosen. On the other hand, even if these results could be used, it is improbable that the theory would account for the large divergences between classical and observed scattering found at these small angles.

Finally it is indicated how the field, when determined, may be applied to the calculation of the energy of binding of two α-particles to form a stable nucleus, of mass number 8, but, as the results so obtained are not in good agreement with what is to be expected, it therefore seems that although this type of field is well adapted to the explanation of scattering phenomena, it is not so successful when applied to the problem of binding.

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* Sexl, 'Z. Physik,' vol. 56, p. 62 (1929).

† Rutherford and Chadwick, 'Phil. Mag.,' vol. 4, p. 605 (1927).

§ 2. We denote the potential energy of an α-particle in the field of a nucleus of atomic number Z by V, and then the field of fig. 1 is expressed mathematically by

$$\left.\begin{aligned} V &= -d & r &< a \\ V &= \frac{2Z\varepsilon^2}{r} & r &> a \end{aligned}\right\}. \qquad (1)$$

The wave equation for an α-particle of mass m_1 moving in the field of such a nucleus of mass m_2 is

$$\frac{1}{m_1}\nabla_1{}^2\psi + \frac{1}{m_2}\nabla_2{}^2\psi + \frac{8\pi^2}{h^2}(E - V)\psi = 0,$$

where, if $\mathbf{r}_1$ and $\mathbf{r}_2$ are the co-ordinates of the particles, $\psi = \psi(\mathbf{r}_1, \mathbf{r}_2)$, and where $\nabla_1{}^2$ and $\nabla_2{}^2$ denote differentiation with respect to $\mathbf{r}_1$ and $\mathbf{r}_2$ respectively. We now put

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2,$$

$$R = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2},$$

$$M^* = \frac{m_1 m_2}{m_1 + m_2},$$

and

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_R(R) \,.\, \psi_r(\mathbf{r}),$$

and the wave equation then resolves in the ordinary way into the two equations

$$\left.\begin{aligned} \nabla_R{}^2\psi_R + \frac{8\pi^2(m_1 + m_2)}{h^2}E_R\psi_R &= 0 \\ \nabla_r{}^2\psi_r + \frac{8\pi^2 M^*}{h^2}(E_r - V)\psi_r &= 0 \end{aligned}\right\}, \qquad (2)$$

where E_R denotes the energy of the whole mass of the system moving with the velocity of the centre of gravity, and E_r denotes the energy of motion of the particles relative to the centre of gravity, so that $E_R + E_r = E$.

The first of these equations gives the motion of the centre of gravity of the system and need not concern us further; the second gives the motion of either particle relative to the other, in terms of the motion of a particle of mass M* relative to a fixed centre of force with a potential V and an energy E_r.

If the problem is now restricted to the case of the bombardment of helium nuclei at rest by a stream of α-particles with velocity v, the centre of gravity of the system consisting of one α-particle and one nucleus may be brought to rest by imposing on the whole system a velocity $\frac{1}{2}v$ in the direction opposite to the direction of bombardment. Then, since the vector joining the centre of gravity to the α-particle is $\frac{1}{2}\mathbf{r}$ (as defined above) the second of equations (2) gives the motion of the α-particles in this new system. In fig. 2, the paths of the two members of such a system are shown, each member being deflected through an angle θ from its original path. The actual motion of each member after the collision is, of course, obtained by again compounding the velocity $\frac{1}{2}v$ which was subtracted, and, as is shown in fig. 2, the angle ϕ through which the incident α-particle is deflected is given by the relation $\phi = \frac{1}{2}\theta$.

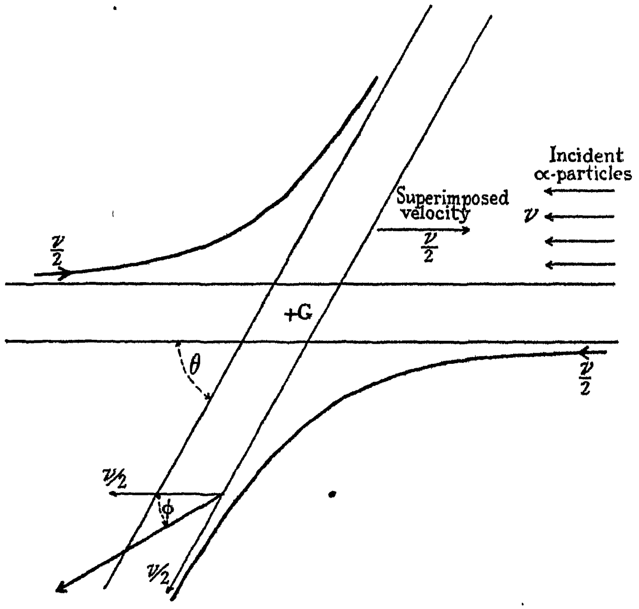

FIG. 2.

In practice, scintillations are counted on a screen placed in a position corresponding to a given deflection ϕ for the incident α-particles, but since the α-particles and the struck helium nuclei are identical, an observed scintillation may be due to an α-particle deflected (in terms of fig. 2) through an angle θ or to a nucleus deflected through an angle $\pi - \theta$. Thus we must use the second of equations (2) to determine the function $f(\theta)$ such that $|f(\theta)|^2$ gives the probability of deflection of an α-particle through an angle θ, and then, on account of the identity of α-particles and helium nuclei and the fact that they obey Einstein-Bose statistics, the probability of scintillations in a direction ϕ will be

$$|f(\theta)+f(\pi-\theta)|^2,$$

where $\theta = 2\phi$. Thus the number of scintillations observed in the range of angles between θ and $d\theta$ is

$$B\,|f(\theta)+f(\pi-\theta)|^2 \,.\, 2\pi\sin\theta\,d\theta$$

or

$$B\,|f(2\phi)+f(\pi-2\phi)|^2 \,.\, 2\pi \,.\, 2\sin\phi\cos\phi \,.\, 2d\phi,$$

where B is a constant readily expressible in terms of Z, ε, and the number of helium nuclei per unit area of struck surface.

If then the number of scintillations observed in solid angle $d\omega$ about the direction ϕ is denoted by $F(\phi)d\omega$, we have, since $d\omega = 2\pi\sin\phi\,d\phi$, that

$$F(\phi) = B\,|f(2\phi)+f(\pi-2\phi)|^2 \,.\, 4\cos\phi.$$

But on the classical theory, it is shown* that, for a Coulombian field,

$$F(\phi) = B\,(\operatorname{cosec}^4\phi + \sec^4\phi)\,4\cos\phi.$$

Hence if we denote by R the ratio of the number of observed scintillations to the number calculated classically from the inverse square law, we have that

$$R = \frac{|f(2\phi)+f(\pi-2\phi)|^2}{\operatorname{cosec}^4\phi+\sec^4\phi}. \tag{3}$$

The experimental values of R for given ranges of ϕ and varying velocities of the incident α-particles are given by Rutherford and Chadwick,† and the graphs I and II of fig. 3 have been drawn from their data. The velocities of the α-particles are expressed as fractions of the velocity, v_0, of the α-particles from R*a*C, namely $1{\cdot}922 \times 10^9$ cm./sec. In the experiments, fairly large ranges of the angle ϕ were used, but the single value assigned to each of the curves is the mean value chosen so that it divides the corresponding experimental range into two parts each of which contains an equal number of scattered particles (assuming the Rutherford law to hold). The dotted curves I*a* and II*a* will be explained below (see p. 112).

It will be observed that whereas the curve I is extended to values of v/v_0 as low as $0{\cdot}55$, the curve II stops short at $v/v_0 = 0{\cdot}70$. The original experiments of Rutherford and Chadwick were conducted with faster α-particles only, and a later† series of experiments, for scattering at 45° only but with slower α-particles, provided the data for the extended part of curve I.

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* Rutherford, Chadwick and Ellis, "Radiations from Radioactive Substances," p. 262.

† Rutherford and Chadwick, *loc. cit.*

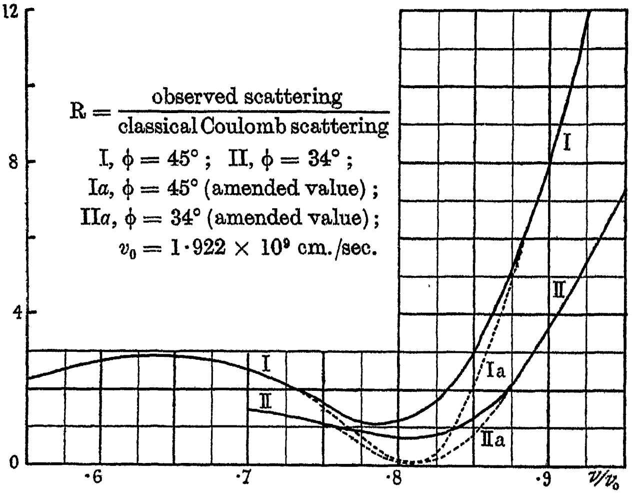

Fig. 3.

In order to determine the value of $f(\theta)$ for the potential field $t\,q\,v\,w\,x$ of fig. 1, we must now investigate the solution of the second of the equations (2) for the values of V given by (1). The general solution of this equation is

$$\psi = \sum_{n=0}^{\infty} \mathrm{A}_n \mathrm{P}_n (\cos\theta)\, \mathrm{L}_n(r), \tag{4}$$

where the A_n are arbitrary constants, and the L_n are solutions of

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\mathrm{L}_n}{dr}\right) + \left\{\frac{8\pi^2\mathrm{M}^*}{h^2}(\mathrm{E}_r - \mathrm{V}) - \frac{n(n+1)}{r^2}\right\}\mathrm{L}_n = 0. \tag{5}$$

For the case of $r < a$, where $\mathrm{V} = -d$, the solution of (5) which is bounded at the origin is well known to be

$$\mathrm{L}_n{}^0(r) = r^{-\frac{1}{2}}\, \mathrm{J}_{n+\frac{1}{2}}(k'r),$$

where

$$\frac{8\pi^2\mathrm{M}^*}{h^2}(\mathrm{E}_r + d) = k'^2.$$

In general, the equation (5) has two independent solutions, and for the case $r > a$ where $\mathrm{V} = 4\varepsilon^2/r$, we shall denote these two solutions by $\mathrm{L}_n{}^1(r)$ and $\mathrm{L}_n{}^2(r)$. There are two special combinations of these solutions which we shall consider further. Let us denote by $\mathrm{L}_n{}^c$ that combination $(\alpha\mathrm{L}_n{}^1 + \beta\mathrm{L}_n{}^2)$

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† J. Chadwick, 'Proc. Roy. Soc.,' A, vol. 128, p. 114 (1930).

which is finite at the origin, and by L_n^s that combination $(\gamma L_n' + \delta L_n^2)$ which for $r = a$ has the same amplitude and gradient as the solution L_n^0. Thus if in (4) we substitute L_n^c, we obtain a wave function for a purely Coulombian field, while if we substitute L_n^s we obtain a wave function in the region $r > a$ for the field of equations (1).

The constants A_n have still to be determined in each case so that the general wave function may represent an incident plane wave together with a spherical scattered wave. For the case of the pure Coulombian field, the constants have been so determined by Gordon,† and if we denote these constants by A_n^c, he shows that

$$A_n^c = \frac{1}{k} i^n (2n + 1) e^{i\sigma_n}, \tag{6}$$

where

$$k = 2\pi M^* v/h,$$

$$1/a = 4\pi M^* . 4\varepsilon^2/h^2,$$

and

$$\sigma_n = \arg \Gamma(i/ak + n + 1).$$

Gordon also shows that the functions $L_n^{1,2}$ and L_n^c have the asymptotic forms

$$L_n^{1,2} \sim r^{-1} e^{\pm i(kr - \frac{1}{2}(n+1)\pi - 1/ak . \log 2rk + \sigma_n)},$$

and

$$L_n^c \sim r^{-1} \cos\left(kr - \frac{n+1}{2}\pi - \frac{1}{ak}\log 2kr + \sigma_n\right), \tag{7}$$

and finally he obtains an asymptotic summation for the wave function

$$\psi^c = \Sigma A_n^c P_n(\cos\theta) L_n^c(r)$$

in the form

$$\psi^c \sim e^{i(kr\cos\theta + 1/ak . \log 2kr \sin^2 \frac{1}{2}\theta} + \frac{e^{i(kr - 1/ak . \log 2kr \sin^2 \frac{1}{2}\theta + \pi + 2\sigma_0)}}{2k^2 ar \sin^2 \frac{1}{2}\theta}. \tag{8}$$

The relation (8) thus represents the incident and scattered waves, in the case when the field is Coulombian, and we have now to find what modification is required when the field is changed to that of equations (1); that is, we have to find a similar asymptotic summation for the wave function

$$\psi^s = \Sigma A_n^s P_n(\cos\theta) L_n^s(r).$$

Now it is clear that L_n^s will have the asymptotic form

$$L_n^s \sim r^{-1} \cos\left(kr - \frac{n+1}{2}\pi - \frac{1}{ak}\log 2kr + \sigma_n + K_n\right), \tag{9}$$

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† Gordon, 'Z. Physik,' vol. 48, p. 180 (1928).

since the only effect of combining in different proportions the two exponential constituents, L_n^1 and L_n^2, of (7) is to alter the phase of the resulting cosine term. This phase change we have denoted by K_n, and the problem now is to determine the values of these constants K_n.

Let us consider for a moment the functions defined by the wave functions multiplied by the distance r. These functions obey the same boundary conditions as do the wave functions themselves, and we have seen that, for a constant potential, the wave function L_n^0 is $r^{-\frac{1}{2}} J_{n+\frac{1}{2}} (k'r)$, and so $r L_n^0$ is $r^{\frac{1}{2}} J_{n+\frac{1}{2}} (k'r)$. Now an inspection of graphs of the Bessel functions of half-integral order will show that all except the first (*i.e.*, $n = 0$) increase very slowly from zero as r increases, and that, the larger is n, the more slowly do they increase, and so the function $r L_n^0$ will have similar properties. Now it is justifiable to assume that the wave functions for a Coulombian field behave in much the same way, and so that for small radii $r L_n^c (r)$ is small if n is large, and becomes smaller as n increases. Now the change of phase, K_n, required to change from $L_n^c (r)$ to $L_n^s (r)$ is dependent, as we have shown, on the amount of difference at $r = a$ between $r L_n^c (r)$ and $r L_n^0 (r)$ and between their derivatives and, since a is small, both these functions and their derivatives are small for large n, and so their difference is small and K_n is small. Hence we may expect that only the first few K will be of importance.

It will be shown below (see pp. 111 and 119) that there are two independent *a posteriori* arguments to show that, for the actual field and the velocities of the incident α-particles with which we are concerned, all the K_n are negligible except K_0 and K_1. Further, since we have seen above that the scattering function is determined by

$$|f(\theta) + f(\pi - \theta)|^2$$

by virtue of the Einstein-Bose statistics, and since $P_n (\cos \theta) = -P_n (\cos (\pi - \theta))$ for all odd values of n, we see that the odd terms of the expansions of ψ^c and ψ^s will not occur in the scattering function.

Thus, finally, the only phase constant with which we are concerned is K_0, and so the value of ψ^s is obtained from that of ψ^c by simply changing $A_0^c L_0^c$ into $A_0^s L_0^s$, giving,

$$\psi^s = \psi^c - A_0^c L_0^c + A_0^s L_0^s. \tag{10}$$

Now since ψ^c itself represents the incident wave and a scattered wave, $A_0^s L_0^s - A_0^c L_0^c$ must represent a scattered wave only; that is, it must be a function of e^{ikr} only, and not of e^{-ikr}. This at once gives

$$A_0^s = A_0^c e^{iK_0} = \frac{1}{k} e^{i(K_0 + \sigma_0)},$$

and so $A_0^s L_0^s - A_0^c L_0^c$ becomes

$$\frac{(e^{2i\mathrm{K}_0} - 1)\, e^{i(kr - 1/ak\,.\,\log 2kr + 2\sigma_0)}}{2ikr}.$$

Hence the part of ψ^s which represents the scattered wave may be written

$$-\frac{e^{i(kr - 1/ak\,.\,\log 2kr + 2\sigma_0)}}{2k^2ar}\{\operatorname{cosec}^2 \tfrac{1}{2}\theta\, e^{-i/ak\,.\,\log \sin^2 \frac{1}{2}\theta} + iak\,(e^{2i\mathrm{K}_0} - 1)\}.$$

Hence we have

$$f(\theta) = e^{i(kr - 1/ak\,.\,\log 2kr + 2\sigma_0)}\{\operatorname{cosec}^2 \tfrac{1}{2}\theta\, e^{-i/ak\,.\,\log \sin^2 \frac{1}{2}\theta} + iak\,(e^{2i\mathrm{K}_0} - 1)\},$$

and so

$$\begin{aligned}|f(\theta) + f(\pi - \theta)|^2 = |\operatorname{cosec}^2 \tfrac{1}{2}\theta\, e^{-i/ak\,.\,\log \sin^2 \frac{1}{2}\theta} &+ \sec^2 \tfrac{1}{2}\theta\, e^{-i/ak\,.\,\log \cos^2 \frac{1}{2}\theta} \\ &+ 2iak\,(e^{2i\mathrm{K}_0} - 1)\,|^2.\end{aligned} \tag{11}$$

Thus for scattering at $\phi = 45°$ we have, from (3) and (11),

$$\begin{aligned}\mathrm{R} &= 2\,\frac{|\operatorname{cosec}^2 \phi + iak\,(e^{2i\mathrm{K}_0} - 1)\, e^{i/ak\,.\,\log \sin^2 \phi}\,|^2}{\operatorname{cosec}^4 \phi}, \\ &= 2\,|\,1 + iak \sin^2 \phi\,(e^{2i\mathrm{K}_0} - 1)\, e^{i/ak\,.\,\log \sin^2 \phi}\,|^2.\end{aligned} \tag{12}$$

From this formula and the values of R for $\phi = 45°$ in fig. 3, values of K_0 were calculated for each value of v, and these values are shown in fig. 4 by the points marked with a cross. Values of K_0 were also calculated for the case $\phi = 34°$ using the more general formula (11) and the curve II of fig. 3, and these are shown in fig. 4 by the points marked with a circle. It is of interest to note that since $\mathrm{P}_2(\cos\theta) = 0$ for $\theta = 54°\ 47'$, the term in K_2 would be zero in the case of $\phi = 27°\ 23'$ and would be small at $\phi = 34°$ even if K_2 were not itself negligible. Hence the good agreement between the values of K_0 as calculated from $\phi = 45°$ and $\phi = 34°$ provides one proof that K_2 is actually negligible.

It may also be mentioned that for values of R greater than about 11, *i.e.*, for v/v_0 greater than about 0·925, the equation for K_0 was found to have no real solution, that is, the phase change K_0 by itself is unable to account for the very largest values of the anomalous scattering. This is in agreement with the fact that K_2 increases as v increases, and it will be shown below that at about the value 0·95 for v/v_0 we would expect the term K_2 to begin to make itself felt.

It will be observed, in fig. 4, that to each value of the velocity there correspond two values of K_0, these two sets of values being shown by the dotted curves I and II. But it is, of course, necessary to choose the set of values which, for small values of v/v_0, tends to the value $K_0 = 0$, since for slow α-particles, the scattering is Coulombian. Again, since the divergence of the potential field from a Coulomb one is such as to make the wave-length of the wave function for $r < a$ less than the wave-length in the Coulomb field, it is clear that for large values of v/v_0 we shall require a positive K_0. Hence it becomes necessary to suppose that the two sets of values of K_0 are in reality cross-connected as is shown by the unbroken lines III and IV. The actual values of K_0 which provide the solution to our problem are then the values given by the bolder of these two lines, namely the curve III.

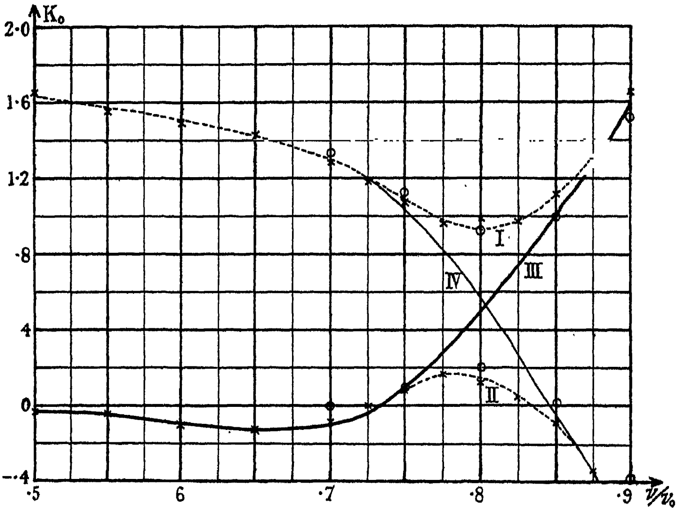

FIG. 4.

In order to justify the modification of the values of K_0 in this way, a calculation was made to determine the values of R corresponding to points on these curves III and IV, and these amended values of R are shown by the dotted curves I*a* and II*a* of fig. 3. It will be observed that the divergence from the experimental values of R is appreciable only when R is itself small, and so when the number of scintillations counted is small, and the probability of error therefore large. Thus it is reasonable to suppose that the divergence between the curves I and I*a*, II and II*a*, of fig. 3, is due to experimental error, and that the variation of K_0 with v is that given by the curve III of fig. 4.

§ 3.—*The Solution of the Wave Equation.*—We have now to introduce the condition that ψ and its derivative shall be continuous as we cross the boundary $r = a$. In assuming $K_n = 0$ for $n \geqslant 2$ we have postulated that this boundary condition is automatically satisfied for all except the first two terms of the resolution (4) of ψ. Further, since the phase K_1 of $L_1{}^s$ does not concern us, it is necessary only to make the values of $L_0{}^s$ and its derivative, at $r = a$, equal to the corresponding values for the wave function for $r < a$, namely, $L_0{}^0$ and its derivative, at $r = a$. The function $L_n{}^0$, which is in general a Bessel function, takes the simple form $r^{-1} \sin k'r$ when $n = 0$.

The differential equation for $L_0{}^s$ is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d L_0}{dr}\right) + \left(k^2 - \frac{2}{ar}\right) L_0 = 0,$$

which, if we write $rL_0 = y$ and $kr = \rho$, may be simplified to the form

$$\frac{d^2y}{d\rho^2} + \left(1 - \frac{2}{ak\rho}\right) y = 0. \tag{14}$$

Sexl* has given the two solutions of this equation and also their asymptotic forms. If y_1 and y_2 are the two solutions, he shows that $y_2 = \bar{y}_1$, where $\bar{y}_1$ denotes the complex conjugate of y_1, and that

$$y_1 = e^{i\rho}\left[1 + \sum_{n=1}^{\infty} (-2i\rho)^n\, a_n\, (b_n + \log - 2i\rho)\right], \tag{15}$$

where

$$a_n = \frac{\Gamma(n + i/ak)}{\Gamma(n)\,\Gamma(n+1)\,\Gamma(i/ak)},$$

and

$$b_n = \sum_{l=1}^{n} \frac{1}{i/ak + l - 1} + \frac{\Gamma'(i/ak)}{\Gamma(i/ak)} + \frac{1}{n} - 2\sum_{l=1}^{n}\frac{1}{l} + 2C,$$

and where C denotes Euler's constant. For large r, and so for large ρ, he shows that

$$y_1 \sim (-)^{i/ak}\,(2i)^{-i/ak - 1}\,\Gamma(i/ak)\,e^{i(\rho - 1/ak\,.\,\log\rho)}.$$

In these results we have omitted certain real constant factors of each solution, since, as we are going to combine the two solutions in varying proportions, these constant factors are immaterial.

Thus we may write

$$y_1 = \lambda\, e^{ikr}\, g(kr)\, e^{i\theta(kr)}, \tag{16}$$

$$y_1 \sim \mu\, e^{i(kr - 1/ak\,.\,\log 2kr + \eta)}, \tag{17}$$

where λ, μ and η are real constants (for varying r but fixed k) and where $g(kr)$ and $\theta(kr)$ are respectively the modulus and amplitude of

$$1 + \sum_{n=1}^{\infty} (-2ikr)^n\, a_n\, (b_n + \log[-2ikr]).$$

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* Sexl, *loc. cit.*, pp. 80 and 83.

Now the solution $ay_1 + by_0$, which is the solution for the Coulomb field, must vanish at the origin so that L_0^c, which is equal to $r^{-1}(ay_1 + by_2)$ may be finite there. But for $r = 0$, y_1 is obviously real, and so $\theta(kr) = 0$, and thus the solution which vanishes at the origin is given by taking $a = -b$, and is $g(kr)\sin(kr + \theta)$. The asymptotic form of this solution is at once seen to be $\sin(kr - 1/ak \,.\log 2kr + \eta)$. Now the asymptotic solution L_0^s for the field of equations (1) is obtained by increasing the phase of the solution L_0^c by the amount K_0, and so the asymptotic form of rL_0^s is

$$\sin(kr - 1/ak \,.\log 2kr + \eta + K_0),$$

and to obtain this solution we must put $a = e^{iK_0}$ and $b = e^{-iK_0}$, and this is at once seen to give $g(kr)\sin(kr + \theta(kr) + K_0)$ as the solution for small r.

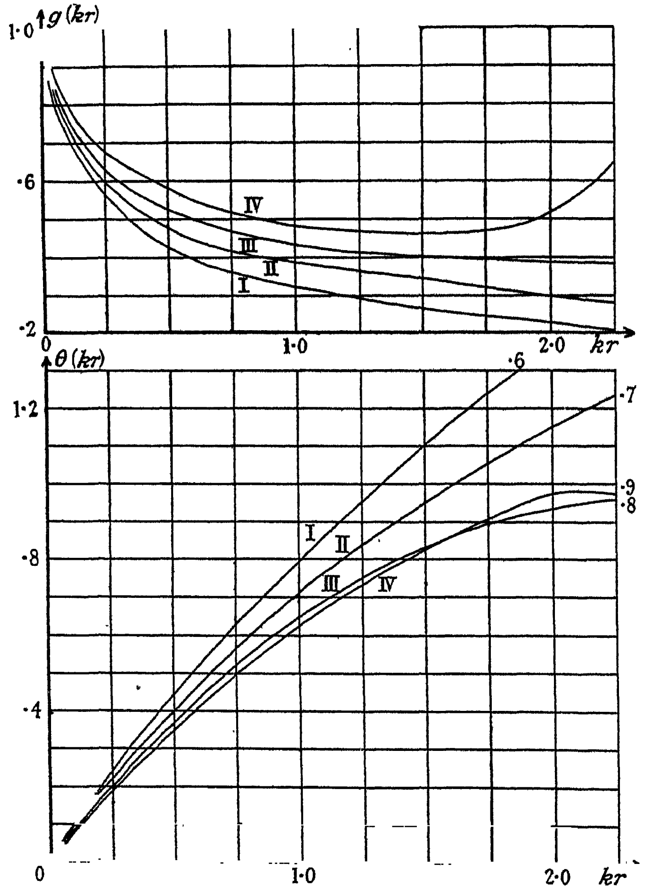

FIG. 5.

This then is the function whose magnitude and derivative must be proportional, at $r = a$, to those of the function $\sin k'r$ which is the solution (rL_0^0)

in the region $r < a$. The fitting of these two functions serves to determine the parameters a and d.

The value of y_1 was calculated from formula (15) for the four values of k corresponding to $v/v_0 = 0 \cdot 6$, $0 \cdot 7$, $0 \cdot 8$ and $0 \cdot 9$, and the corresponding values of $g\,(kr)$ and $\theta\,(kr)$ are shown in fig. 5 for values of kr in the range $0 \leqslant kr \leqslant 2 \cdot 25$. Combining these results with the corresponding values of K_0 from fig. 4, the curves of fig. 6 were drawn, showing $g\,(kr) \sin\,(kr + \theta\,(kr) + K_0)$ plotted

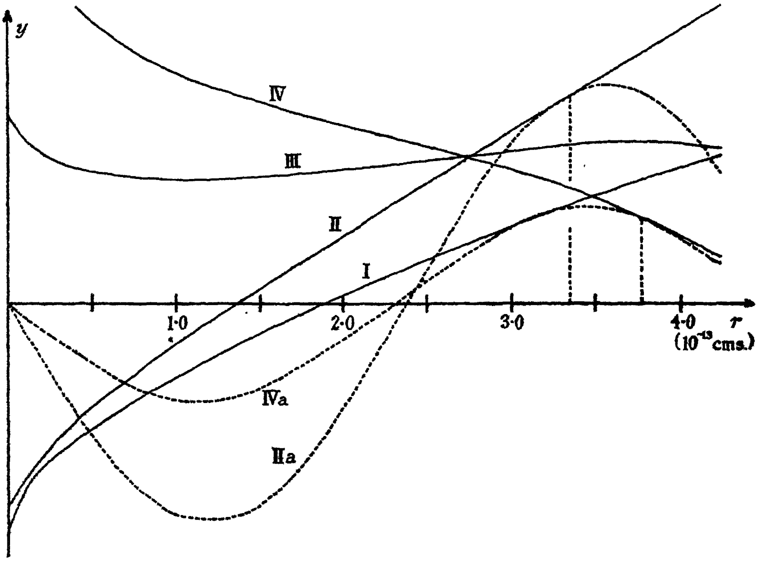

Fig. 6.

I, $y = rL_0{}^s$ for $v/v_0 = 0 \cdot 6$; II, $y = rL_0{}^s$ for $v/v_0 = 0 \cdot 7$; III, $y = rL_0{}^s$ for $v/v_0 = 0 \cdot 8$; IV, $y = rL_0{}^s$ for $v/v_0 = 0 \cdot 9$; II*a*, $y = r\psi_0$ $(r < a)$ for $v/v_0 = 0 \cdot 7$; IV*a*, $y = r\psi_0$ $(r < a)$ for $v/v_0 = 0 \cdot 9$.

against r. These curves show the variation of $rL_0{}^s$ with r for each of the four velocities.

Taking any one of the curves of fig. 6, it is possible to fit a curve $y = \sin k'r$ to it at *any* value of r, by choosing a suitable value of k'. That is to say, we may satisfy the boundary condition with one of these curves, that is with one velocity of α-particles, for *any* value of a; but then, since k' is fixed, the relation

$$k'^2 = k^2 + \frac{8\pi^2 M^* d}{h^2}$$

fixes d. Now the boundary conditions at $r = a$ may be written

$$c \,.\, \sin k'a = g\,(ka) \sin\,(ka + \theta\,(ka) + K_0)$$

$$c \,.\, \frac{k'}{k} \cos k'a = \frac{d}{dka}\,[g\,(ka) \sin\,(ka + \theta\,(ka) + K_0)],$$

and so the relation giving k' in terms of a for any one specified k is

$$\frac{k'}{k}\cot k'a = \frac{1}{f}\frac{df}{dka}, \tag{18}$$

where

$$f = g\,(ka)\sin\,(ka + \theta\,(ka) + \mathrm{K}_0),$$

and then the value of d is determined as above.

From each curve of fig. 6 the value of

$$\frac{1}{f}\frac{df}{dka}$$

can be determined for every value of a, and thus the right-hand side of equation (18) is known for each of the four values of k corresponding to the curves of fig. 6, and for every a. Hence we may solve (18) to determine the corresponding values of k' and then from

$$k'^2 = k^2 + \frac{8\pi^2\mathrm{M}^*d}{h^2},$$

we determine d. The curves of fig. 7 are numbered to correspond with those of fig. 6, and show the way in which a and d vary together when k is constant.

Since, of course, the interaction energy of two α-particles at a given distance apart is a function only of that distance, and not of any original motions of the particles, a and d are constants independent of any variation of k, and so the particular values of a and d which are the solution to our problem are provided by the co-ordinates of any point through which *all* the curves of fig. 7 pass.

It will be observed that, in the range of r from zero up to 4×10^{-13} cm., the curves III and IV are two-branched, while I and II have only one branch. The second branch for I and II does not occur until r reaches values of about 8×10^{-13} cm. The first branches of all four curves tend asymptotically to the axis $r = 0$, corresponding to an infinitely deep "hole" of zero width, but this solution to the problem is of no interest. The next point, at which all four curves pass—approximately—through one point, is given by $a = 3{\cdot}5 \times 10^{-13}$ cm., and by a value of

$$\frac{8\pi^2\mathrm{M}^*d}{h^2},$$

which corresponds to $d = 16 \times 10^6$ electron volts. It is to be remembered that in obtaining the points on the curves of fig. 7 we have first to read a gradient from the curves of fig. 6, and then to solve graphically an equation containing this gradient as one of its terms, and so the curves of fig. 7 are liable to considerable experimental error and are not to be expected to pass more accurately than they do through one point.

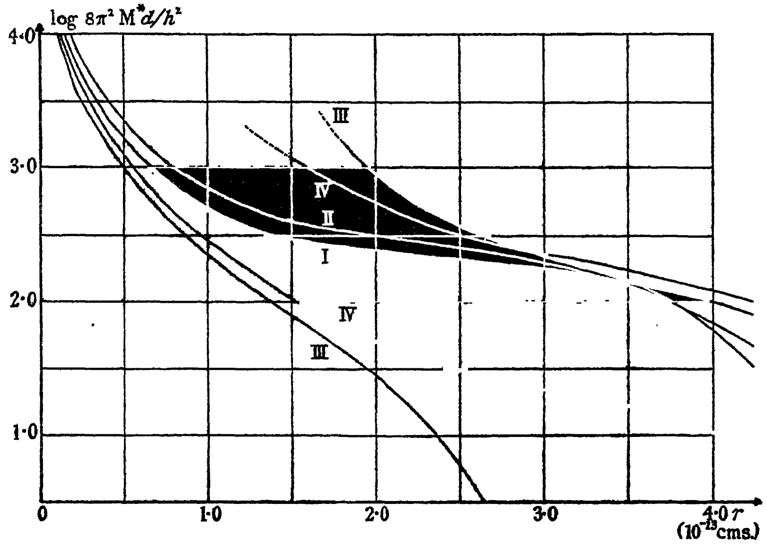

FIG. 7.

I, $v/v_0 = 0\cdot6$; II, $v/v_0 = 0\cdot7$; III, $v/v_0 = 0\cdot8$; IV, $v/v_0 = 0\cdot9$.

By trial and error methods it was then found that $d = 15\cdot6 \times 10^6$ electron volts was the value which gave the least variation in the value of a for different values of the velocity v. In Table I are given the values of k, k' and a which for this value of d correspond to the velocities of the curves I to IV of fig. 6, while in fig. 6 itself the two dotted curves II*a* and IV*a* show the functions $\sin k'r$ inside the "hole" fitted to the external functions. These curves are shown for II and IV only, so as to avoid confusing the figure, but the points of fitting (*i.e.*, the values of a) for the other two curves lie within the two dotted ordinates for which fitting occurs with these curves.

Table I.—$d = 15\cdot6 \times 10^6$ electron volts.

v/v_0.	k.	k'.	a.
	cm.$^{-1}$	cm.$^{-1}$	cm.
0·6	$3\cdot66 \times 10^{12}$	$13\cdot0 \times 10^{12}$	$3\cdot35 \times 10^{-13}$
0·7	$4\cdot27 \times 10^{12}$	$13\cdot2 \times 10^{12}$	$3\cdot35 \times 10^{-13}$
0·8	$4\cdot88 \times 10^{12}$	$13\cdot4 \times 10^{12}$	$3\cdot45 \times 10^{-13}$
0·9	$5\cdot49 \times 10^{12}$	$13\cdot6 \times 10^{12}$	$3\cdot75 \times 10^{-13}$

§ 4. ***Results.***—In fig. 8 the potential energy of an α-particle in the field of another is plotted to scale, using $3 \cdot 5 \times 10^{-13}$ cm. as the mean value of a, and

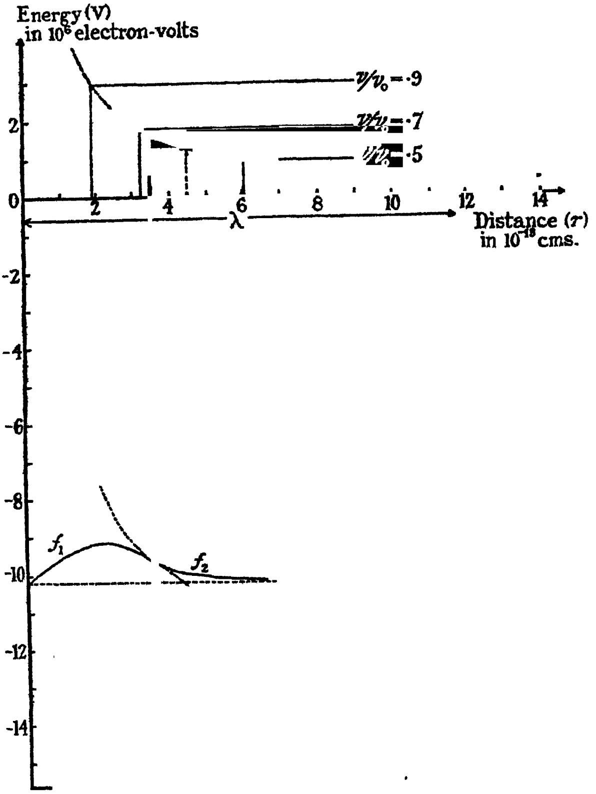

FIG. 8.—The energy of one α-particle in the field of another. N.B.—It is to be emphasised that this figure does not show the electrostatic potential of one α-particle, but the mutual energy of two.

$15 \cdot 6 \times 10^6$ electron volts for d. The three horizontal lines show the energies E_r (equation (2)) of the α-particles for which v/v_0 has the values $0 \cdot 5$, $0 \cdot 7$ and $0 \cdot 9$, and the three corresponding ordinates therefore show the classical distances of closest approach in a direct collision. It will at once be remarked that the lowest velocity for which the α-particle enters the region of divergence from the Coulomb law (*i.e.*, v/v_0 about $0 \cdot 7$) is of the same order as the velocity for which in fig. 3 the scattering at 45° begins to differ markedly from twice classical. That is to say, that the anomaly in scattering due to the field being non-Coulombian appears at about the same velocity as that at which, on the classical theory, the α-particle can enter the region of non-Coulombian field.

The twice classical scattering referred to above is, of course, due to the identity of α-particles and helium nuclei, an effect first predicted by Mott.†

It is of interest also to remark how large the value of the negative energy must be inside the "hole" in order to account for the scattering. The distance λ shown in fig. 8 is the wave-length of the α-particles of velocity $0 \cdot 9v_0$, and as this is the shortest wave-length considered, it is interesting to consider how large it is compared with the width of the "hole." It might also be pointed out that by virtue of the fact that the collision is a two-body problem (the struck nucleus being light) the energy E_r is given by $\frac{1}{2}M^*v^2$ and the wave-length λ by h/M^*v, and so the first is just half and the second just double what they would be were the struck nucleus infinitely heavy.

The region in which the law of force is non-Coulombian having been determined, it becomes possible to check the assumption that the second and higher terms of the resolution (4) do not have their phases changed from the Coulombian value. The physical interpretation of the resolution of the plane wave into a series of spherical harmonics of order 0, 1, 2, ... is a resolution of the incident beam of α-particles into a set of quantised streams with angular momenta 0, 1, 2, ... times $h/2\pi$ about the nucleus. Thus we may at once determine the classical distance of closest approach for the particles corresponding to each spherical harmonic. The phase change K_0 became appreciable only when the α-particles corresponding to the zero order harmonic, *i.e.*, those suffering direct collision, had a high enough velocity to make the classical distance of closest approach lie inside the region of non-Coulomb field, and it is reasonable to suppose the same true for the higher terms. In Table II are shown the impact parameters‡ and classical distances of closest approach for α-particles of velocities $0 \cdot 90v_0$ and $0 \cdot 95v_0$.

Table II.

	$v/v_0 = 0 \cdot 9$.		$v/v_0 = 0 \cdot 95$.	
	Impact parameter.	Closest approach.	Impact parameter.	Closest approach.
	cm.	cm.	cm.	cm.
First harmonic	$1 \cdot 83 \times 10^{-13}$	$2 \cdot 98 \times 10^{-13}$	$1 \cdot 73 \times 10^{-13}$	$2 \cdot 76 \times 10^{-13}$
Second harmonic	$3 \cdot 66 \times 10^{-13}$	$4 \cdot 71 \times 10^{-13}$	$3 \cdot 47 \times 10^{-13}$	$4 \cdot 40 \times 10^{-13}$

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† N. F. Mott, 'Proc. Roy. Soc.,' A, vol. 126, p. 259 (1930).

‡ Andrade, "Structure of the Atom," p. 21.

Thus it will be seen that the phase change K_2 may be expected to be just becoming appreciable for the velocity $0 \cdot 95 v_0$, while for $0 \cdot 90 v_0$ it will be expected to be reasonably small. This is altogether in agreement with our observation that K_0 by itself was unable to account for the large scattering ratio at $0 \cdot 95 v_0$ (p. 111). For all lower velocities, of course, K_2 will be quite negligible. The table also shows that K_1 may be quite large for both these velocities, but we have already seen that K_1 does not affect our results.

The potential field of fig. 8 is admittedly an idealised one, and it is of interest to see to what extent we may expect our results to be modified by a slight alteration of the field. The most obvious modification, and one which makes the field a much more natural one, is to remove the sharp peak at $r = a$ by the dotted line yz (fig. 1), and so obtain the field $t\,z\,y\,w\,x$. The wave functions for this field are :—

$$\psi = \lambda \sin k'r \qquad r < a,$$

$$\psi = \mu \sin (k''r + \phi) \qquad a < r < b,$$

and

$$\psi = \nu\, g(kr) \sin (kr + \theta (kr) + K_0') \quad b < r,$$

where k and k' are as before, and where

$$k''^2 = k^2 - 8\pi^2 M^* c/h^2,$$

the line yz being the line $V = c$ as shown in fig. 1. The boundary condition at $r = a$ at once enables us to find ϕ for any given value of k, *i.e.*, of v, and that at $r = b$ then determines K_0'. In Table III we show values of K_0' so calculated for each of the four velocities used in the above work. The value of a corresponding to each value of v was taken from Table I instead of using a mean value of a, and in each case a length $b - a$ of 1×10^{-13} cm. was cut off from the peak. Beside each value of K_0' is shown the value K_0 which corresponds to the actual scattering, and it will be seen that in each case the difference is immaterial.

Table III.

v/v_0.	K_0'.	K_0.
0·6	−0·09	−0·11
0·7	−0·10	−0·12
0·8	+0·42	+0·46
0·9	+1·56	+1·66

One of the most obvious criticisms of the idealised field $t\,q\,v\,w\,x$ of fig. 1 is the existence of the sharp peak at $r = a$, and we see that we can modify the field to avoid that criticism without materially affecting our results. If the cutting off of the peak by the single horizontal line yz affects the results so little, it is clearly possible to go a stage further and cut off the two corners so produced by slanting lines, and thus ultimately to round off the curve to very much the shape of the original Gamow curve, still keeping the breadth of the large hole at $3 \cdot 5 \times 10^{-13}$ cm.

This result would be most unexpected on the classical mechanics, for cutting off the top of the potential peak would alter materially the velocity at which α-particles would enter the non-Coulombian field, and so would alter in the same way the velocity at which anomalous scattering sets in. On the wave mechanics, however, the change in the field does not make an appreciable change in the wave functions, firstly because the region in which the change is made is small compared with the wave-length of the incident α-particles (see fig. 8, the dotted line shows the extent of peak cut off, and λ is the shortest wave-length used), and secondly because the complete variation in energy outside the hole is so small compared with the depth of the hole that the scattering is determined very largely by the hole and not by any small changes in the outside field.

§ 5. *Prediction of Energy of Binding of two α-Particles.*—When the potential energy of one α-particle in the field of another has been determined as above, it becomes possible to investigate whether there is any eigenvalue of the energy corresponding to a stationary stable state in which the wave function is a sine curve inside the "hole" in fig. 8, and falls away exponentially outside. In order to simplify the calculation of such an eigenvalue, the field of fig. 8 was further idealised by assuming that, for values of r greater than a, V had the constant value $0 \cdot 5 \times 10^6$ electron volts. This would not materially affect the value obtained for the eigenvalue, on account of the comparatively negligible variation of V outside $r = a$ even in the actual field.

The problem, therefore, is to find a value of E such that the two wave functions given by

$$r\psi_1 = f_1 = \sin k_1 r,$$

and

$$r\psi_2 = f_2 = e^{-k_2 r},$$

shall satisfy the usual boundary condition on $r = a$, where k_1 and k_2 are determined by

$$k_1{}^2 = \frac{8\pi^2 M^*}{h^2}(d + E),$$

and

$$k_2{}^2 = \frac{8\pi^2 M^*}{h^2}(0 \cdot 5 \times 10^6 - E).$$

It is readily found that there is only one value of E which satisfies these conditions, and its value (in electron volts) is $-10 \cdot 2 \times 10^6$. This energy level is shown by the dotted horizontal line, and with it as axis are shown the two functions f_1 and f_2.

Thus two α-particles may be combined to form a stable nucleus of mass number 8, and the energy lost, over and above that initially lost in the formation of the α-particles from their constituent protons and electrons, is about 10^7 electron volts, or $3 \cdot 2 \times 10^{-5}$ ergs. This corresponds to a loss of mass of about $3 \cdot 5 \times 10^{-26}$ gms., or to a mass defect from the mass of two α-particles of 0·28 per cent. But the mass defects of carbon (12) and oxygen (16), which presumably consist of three and four α-particles so combined, are respectively 0·02 and 0·05 per cent. when measured in the same way from the mass of three and four α-particles. It seems improbable that the nucleus (8) should differ so widely from those of carbon (12) and oxygen (16) and thus it seems that the field of fig. 8 is more particularly adapted to explain scattering phenomena, and is not so successful in predicting binding energies.

§ 6. *An Alternative Potential Field.*—A further potential field for which the calculation of the wave functions is not unreasonably laborious is that shown in fig. 9. This field is also determined by the two parameters a and d.

For incident α-particles of energy E_r, the wave equation for $r > a$ is the same as before, and so the values of $L_0{}^s$ shown in fig. 6 are still the solutions for $r > a$, but for $r < a$ the wave equation is

$$\nabla^2\psi + \frac{8\pi^2 M^*}{h^2}(E_r + d - br)\,\psi = 0,$$

where b is readily expressible in terms of a, d and $Z\varepsilon^2$. Thus, writing $f = r\psi$, $k^2 = \frac{8\pi^2 M^*}{h^2}(E_r + d)$ and $b' = 8\pi^2 M^* b/h^2$, the wave equation can be expressed as

$$\frac{d^2 f}{dr^2} + (k^2 - b'r)\,f = 0, \qquad (19)$$

where we have assumed spherical symmetry, *i.e.*, have considered only the spherical harmonic term of order zero. If now we put $k^2 - b'r = b'^{2/3}\, y$, the

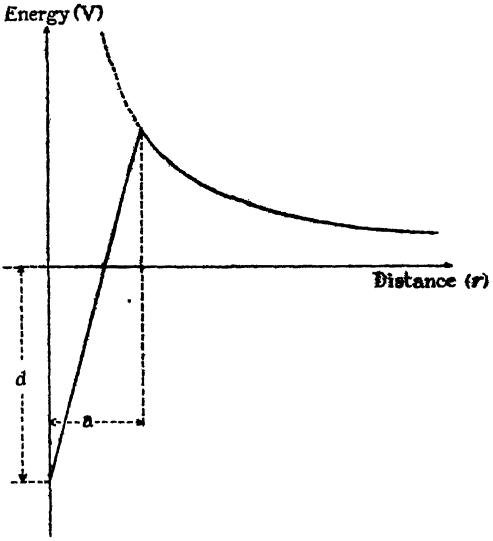

FIG. 9.

solutions of (19) may be shown to be $f_{1,\,2} = y^{1/2}J_{\pm 1/3}\,(\frac{2}{3}y^{3/2})$, and in order to satisfy the condition that ψ is finite at $r = 0$, the proper solution of (19) must be

$$r\psi = \lambda f_1 + \mu f_2,$$

where $\lambda : \mu = -\, J_{-1/3}\,(\frac{2}{3}y_0{}^{3/2}) : J_{+1/3}\,(\frac{2}{3}y_0{}^{3/2})$, y_0 being the value of y when $r = 0$, namely $k^2b'^{-2/3}$.

The curves of fig. 10 showing the two functions $x^{1/2}J_{\pm 1/3}\,(\frac{2}{3}x^{3/2})$ were drawn from the tables of Bessel functions given by Watson,* and from these curves the proper solution, for any given value of E_r, a and d, can be readily constructed. It is not convenient as in the previous case to obtain curves showing the variation of d with a for each value of E_r (*cf.* fig. 7), but, if any special value be assigned to a, it is possible to determine the corresponding value of d for each E_r. The three values 2·5, 3·5 and $4{\cdot}5 \times 10^{-13}$ cm. were tried for a, and in Table IV are shown the corresponding values of d for the values 0·7, 0·8, and 0·9 for v/v_0.

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* G. N. Watson, " Theory of Bessel Functions."

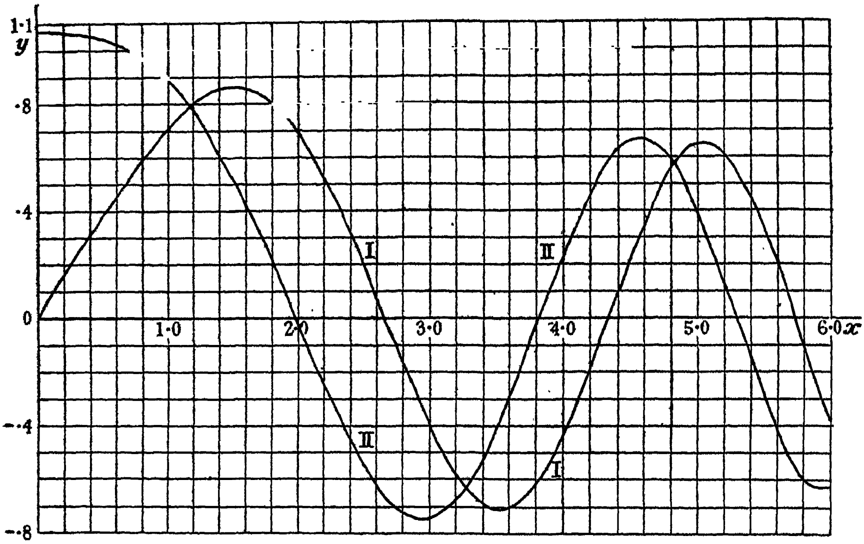

Fig. 10.

I, $y = x^{1/2}J_{1/3}(\frac{2}{3}x^{3/2})$. II, $y = x^{1/2}J_{-1/3}(\frac{2}{3}x^{3/2})$.

Table IV.

	$a=2\cdot5\times10^{-13}$ cm.			$a=3\cdot5\times10^{-13}$ cm.			$a=4\cdot5\times10^{-13}$ cm.		
v/v_0	0·7	0·8	0·9	0·7	0·8	0·9	0·7	0·8	0·9
d (in 10^6 electron volts)	75	95	114	37	43	50	18	22	26

The depths corresponding to the width $2\cdot5\times10^{-13}$ cm. show a variation of 21 per cent. from the mean, those for 3·5 show a variation of 16 per cent., and those for 4·5 a variation of 18 per cent. If this be compared with the variation in width for the case of fixed depth and varying velocity in the field of fig. 8, the results in Table I show an extreme variation of only 7 per cent. from the mean, and so it appears that the actual field is represented more closely by the vertically descending "cut-off" of fig. 8 than by the more gradual one of fig. 9. At the same time, it will be noticed that the percentage variations in Table IV are least for the same value of a as was obtained with the original field, and so to this extent these results lend confirmation to the theory as a whole.

Summary.

It has been shown that the distance between centres of two α-particles at which their interaction energy ceases to be that given by the Coulomb law is about $3 \cdot 5 \times 10^{-13}$ cm. This result has been confirmed with two types of field, but it has been shown that the actual field is more nearly approximated to by fig. 8 than by fig. 9.

It is a pleasure here to acknowledge my indebtedness to Mr. N. F. Mott for helpful advice and criticism throughout the course of this work, and to the Department of Scientific and Industrial Research for a grant which has made the work possible.

The Mobility of Positive Ions in Helium. Part I.—Helium Ions.

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Introduction.

In a previous paper* we gave an account of some experiments on the mobility of positive ions in helium gas. It was shown that minute traces of impurity profoundly affect the speed at which the charge is carried through the gas, so that very little significance can be attached to the values of the mobility of ions recorded in the literature. In particular we studied the behaviour of carefully purified helium gas when admitted at a pressure of 360 mm. of mercury into a baked-out apparatus. In our method of determining the mobility, a single group of ions gives rise to a peak in a current-frequency curve, and it is easy to follow the changes produced by an impurity. Initially the ions in the helium had a high mobility and in one case we obtained a group with a mobility of the order of 17 cm./sec./volt/cm. at 760 mm. As the gas became contaminated by impurities gradually evolved from the glass walls and metal parts of the apparatus, peaks corresponding to groups of smaller mobility appeared, and eventually the charge was all carried by a group with mobility rather less than 8. The ions in these experiments were produced by means of α-particles from polonium.

Traces of impurity in helium may affect the results in several ways. Firstly, they may lead to the formation of ionic clusters, particularly if the molecules of the impurity have a permanent dipole. In our experiments it seemed unlikely that molecules capable of forming clusters were present. Secondly, although with small concentrations of an impurity a negligible number of its ions will be produced by the direct action of the α-rays, they may be formed indirectly in either of the two following ways :—

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* Tyndall and Powell, 'Proc. Roy. Soc.,' A, vol. 129, p. 162 (1930).

(*a*) By collisions of the second kind between metastable atoms of helium and molecules of the impurity.* If an appreciable number were formed in this way we should expect to observe two peaks in our current-frequency curve, one due to helium and one due to impurity. With small traces of impurity the helium ions should predominate in number; they certainly would not be a negligible fraction of the total number. This process then does not account for our previous results, for we found that as the traces of impurity accumulated, the fastest ions disappeared entirely. That it is an important process in the study of the electrical properties of gases is shown by the experiments of Penning† on the effect of traces of impurity on the sparking potential of neon, and of Headrick and Duffendack on the positive column of the glow discharge.‡ In a later paper we shall describe a type of glow discharge for producing impurity ions in the rare gases which is based upon it.

(*b*) By the capture of electrons from impurity molecules by the positive helium ions. The phenomenon of electron capture has been studied experimentally by Kallmann and Rosen§ and others,|| and theoretically by Morse and Stueckelberg.¶ This process would explain the results observed provided that the probability of transfer at a collision and the number of collisions were great enough.

In pure helium the charge does not remain associated with the same atom in its passage through the gas, but passes from one helium atom to another by electron exchange. On the other hand, impurity ions in helium lose their charge very seldom. In any case, at the speeds used in our experiments, a transfer of charge can only take place to other impurity atoms and never back to helium atoms since the energy of the ions is not much greater than the

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* Penning, 'Naturwiss.,' vol. 15, p. 118 (1927).

† 'Phil. Mag.,' vol. 11, p. 961 (1931).

‡ Headrick and Duffendack, 'Phys. Rev.,' vol. 37, p. 736 (1931), and also 'Duffendack and others, 'Phys. Rev.,' vol. 34, pp. 35, 68, 409, 1132 (1929).

§ Kallmann and Rosen, 'Z. Physik,' vol. 61, p. 261 (1930).

|| *Loc. cit.*

¶ Morse and Stueckelberg, 'Ann. Physik,' vol. 9, p. 579 (1931).

thermal energy of the atoms of the gas through which they are moving. Therefore, once an impurity ion is produced it persists and it is for this reason that small concentrations of impurity are so important.

In our previous experiments the difficulties of purification were such that we could not identify any definite group of ions as singly charged helium atoms. Moreover, the apparatus was not adapted for absolute determinations because during a portion of their path the ions travelled in a field, the value of which could only be estimated. In the continuation of these experiments we have made some important modifications.

The apparatus has been adapted for work at lower pressures in order to reduce the effect of small traces of impurity. If we assume that there is some lower limit to the percentage concentration of impurity which can be obtained by a given method of purification, then its absolute concentration is inversely proportional to the pressure. Secondly, with a given field, the speed of the ions, and, therefore, the time they spend in the gas, is inversely proportional to the pressure. In a gas containing a given small percentage of impurity the number of impurity ions formed by electron capture will vary either as the square of the pressure or, if this transfer of charge requires a three-body collision, as the cube of the pressure. We have therefore worked with helium at pressures from 20 to 60 mm. of mercury instead of 360 mm.

At these lower pressures polonium is not suitable as a source of ionisation, partly because of the reduced density of ionisation and partly because of the increased range of the α-particles themselves. We have therefore substituted a glow discharge. Incidentally this change removes another possible source of residual impurity, since it was impossible in the older apparatus to bake out the polonium and its holder without fear of α-ray contamination of the analysing chamber.

The lower pressure involves the use of oscillators of higher frequency than the maximum of 6000 cycles/sec. previously employed. We have now constructed new ones to cover a range up to 50,000 cycles/sec.

In a second form of the apparatus a further modification has been introduced to enable us to obtain absolute values of the mobility.

New Apparatus.

In the experiments described in this paper we have used two new tubes, the first of which is shown in fig. 1. It is similar in principle to that described in the previous paper, which should be consulted for further particulars. The changes in design may be summarised as follows :—

The electrodes are of molybdenum with quartz insulation. The "shutter grids" AB, CD are pierced with 20 holes 0·5 mm. in diameter, the corresponding holes in the four plates being in good alignment. The diameter of the plates is 25 mm., AB=CD=2 mm., BC = 15 mm. The glass work is of "pyrex" so that the apparatus can be given a more rigorous heat treatment than previously, and the leads to the various electrodes are taken out through tungsten wire pinches and seals. The glow discharge is maintained between the point M and a pierced platinum plate N and the ions so formed are dragged by a suitable field up to the analysing part of the apparatus.

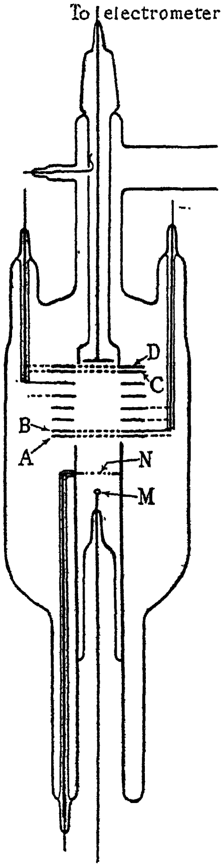

Fig. 1.

It is important that the wave form of the potential fluctuations applied to the shutter grids shall be accurately sinusoidal over the complete range of frequencies delivered by the oscillator. Serious difficulties arise if harmonics are present in the alternating current in the main coil of the oscillator because these may resonate with the natural frequencies of the coupled coils. Since they were made of different sizes, to slide over one another, the two coupled coils have different natural frequencies. We may, therefore, test whether any distortion is introduced at any frequency by the presence of harmonics by applying the potentials from the coils to the two sets of deflecting plates of a cathode ray oscillograph. If they both vary sinusoidally the resulting trace on the oscillograph will be linear, but if a harmonic in the main oscillatory current resonates with the natural frequency of one of the coils the trace is seriously distorted.

To avoid the harmonics, two precautions are necessary. Firstly, the coupled coils must have few turns and therefore a high natural frequency. Secondly, no appreciable grid current may be taken by the valves if the main oscillatory current is to retain an approximation to a sine wave form. For the frequency ranges 1000 to 40,000 cycles/sec., we use oscillators maintained by three Marconi-Osram L.S.5 valves in parallel. The anode potential is 300 volts, the grid bias 30 volts and the anode current 50 milliamperes. With a given value of the capacity of the main oscillatory condenser, the grid coil is brought up towards the anode coil until the anode current changes slightly. The set is then oscillating and the grid current is negligible. If the coupling between the grid coil and the anode coil is much increased beyond this point, grid current begins to flow, and the wave form becomes distorted. With these precautions we have obtained good sinusoidal alternating potentials in both the coupled coils over the entire frequency range of our oscillators.

The frequency delivered by the oscillator with different values of the capacity of its condenser was measured by means of the cathode ray oscillograph. Across one pair of plates the frequency to be measured was applied; across the other pair an alternating potential of known audible frequency, to serve as a time base. The capacity of the condenser was decreased gradually and a simple pattern of the expected form was produced on the oscillograph screen when the frequency of one oscillator was an integral multiple of that of the other. In this way we have compared frequencies with ratios up to seventy to one and have thus deduced the frequency of the oscillations for any given setting of the condenser.

Preparation of the Pure Gas.

In the previous work the helium, stated to be of 99 per cent. purity, was obtained from a cylinder. It was further purified by heated copper oxide, sodium glow discharge and charcoal cooled in liquid air. In the present work the helium was obtained from thorianite and we are indebted to Mr. S. P. MacCallum for a supply of this mineral in powdered form. The thorianite was heated for an hour at 700° C. in a silica tube to drive off water and organic vapours. The tube was then exhausted and heated to 950° C. to drive off the helium. The helium, which comes off steadily at this temperature, was passed over potash and phosphorus pentoxide into an exhausted reservoir and then purified by the method previously described. Before the introduction of the gas, the main apparatus was exhausted for many hours at 550° C. When, after admission, the gas was subjected to an electrodeless discharge and examined spectroscopically no lines other than those of helium were found.

Resolving Power.

The power of the apparatus to resolve groups of ions of different mobility is limited only by the width of the pulse of ions allowed to pass through the shutters, and by the diffusion of the ions. Also, if in different experiments, the fields between the several electrodes are all changed in the same ratio, a single group of ions always gives rise to a peak in the current-frequency curve of a given standard form. The resolving power of the new apparatus is illustrated in figs. 2 and 3. Fig. 2, A, is a typical result in pure helium. Fig. 2, B, was obtained in helium containing mercury vapour at a concentration of 1 in 70,000, admitted by removing a liquid-air trap.* The peak at the lower frequency could be produced or suppressed at will by admitting or freezing out the mercury. The helium in this case had been in the apparatus for some days and the small hump in the figure between the two main peaks is no doubt the result of slight contamination by some impurity evolved from the walls.

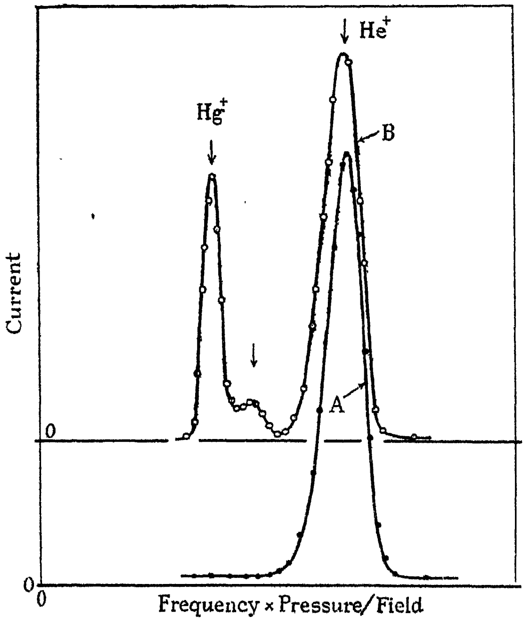

Fig. 2.—Curve A, Pure Helium at 38 mm. Curve B, Helium at 53 mm., containing mercury vapour at 0·0008 mm.

Results which we have obtained in the other rare gases will be described in a subsequent paper, but as illustrations of resolving power we reproduce two curves obtained in krypton which was known to be slightly impure. Fig. 3, A, was taken immediately after the introduction of the gas. It gives definite evidence of three, if not four, groups of ions, indicated by arrows. Fig. 3, B, was obtained after the gas had been subjected to an intense electrodeless discharge for 3 hours. It will be seen that four groups of ions are present at approximately the same frequencies as before but in entirely different proportions.

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* This particular curve was actually obtained with a glow discharge of different type from that shown in fig. 1. A discussion of the conditions necessary for the production of impurity ions is reserved for a later paper.

Certain conclusions important to the work on helium can be drawn from these results. Firstly, they illustrate the efficiency of the method in detecting groups of ions of different mobility. Secondly, they show what misleading conclusions might be drawn from results by earlier methods only capable of detecting the ion present in largest quantity. Thirdly, Penning and also MacCallum have shown, in work on sparking potentials, the marked effect of glow discharge in cleaning up residual traces of impurity, presumably by ionising them and driving them temporarily into the walls. The fact that fig. 2, A, for pure helium gives a single peak, unaltered in height and position by electrodeless discharge, enables us to say with confidence that we are dealing with positive ions of helium moving in helium gas, and unaffected by impurity.

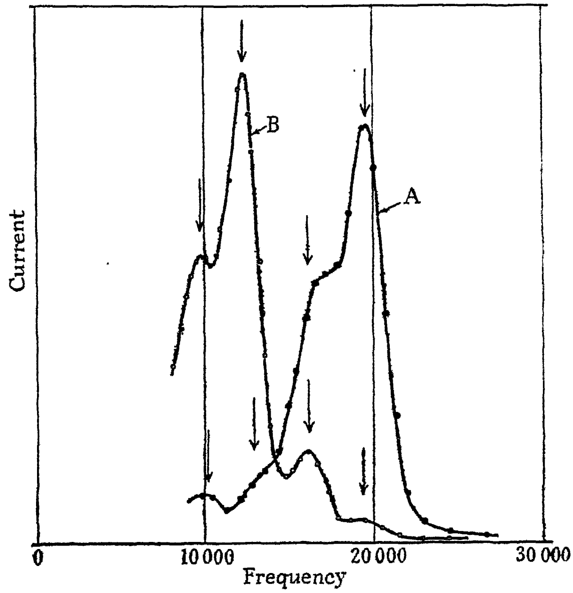

Fig. 3.—Krypton at 4·86 mm. Peaks in 2nd order. Alternating Potentials out of phase.

Effect of Pressure.

From early work on the effect of pressure, Langevin and others concluded that the mobility of an ion was inversely proportional to the pressure. But it is now clear that in their experiments the gas was not of sufficient purity to obtain the ions in their simplest form. If in a pure gas the ions are single atoms or molecules, one cannot assume Langevin's law without further evidence. Indeed, more recently, from some experiments in corona discharge in helium and neon, Huxley* concluded that the velocity of the positive ions was not in general proportional to E/p where E is the field in volts/cm. and p the pressure in millimetres. In helium the proportionality held up to a value of E/p equal to 2 and then broke down. In neon the velocity was a linear function of E/p but not proportional to it.

Curves of the type fig. 2, A, have therefore been obtained for a number of different pressures from 20 to 80 mm. In our method, if the speed of the ion is proportional to E/p then the quantity fp/E, where f is the peak frequency, should be a constant at all pressures. The results are shown in fig. 4 in which this ratio is plotted with pressure. The field in these experiments was of the order of 84 volts/cm. and the results therefore show in disagreement with Huxley that the ratio fp/E is independent of pressure over a range of E/p up a value of 4·2. In other words, Langevin's law may be applied at least over this range and the values of mobility at different pressures may all be reduced to a standard value at atmospheric pressure by multiplying them by the factor P/760. Assuming that the speed of other positive ions is also proportional to E/p, this apparatus, although it does not give absolute values, enables us to obtain accurate relative values of their mobilities. All that is necessary is to select values of pressure and field so that the peak frequency falls within the range of oscillator. Then for a given ion fp/E will be constant and the ratio of the values of this quantity for two different ions will be the ratio of their mobilities.

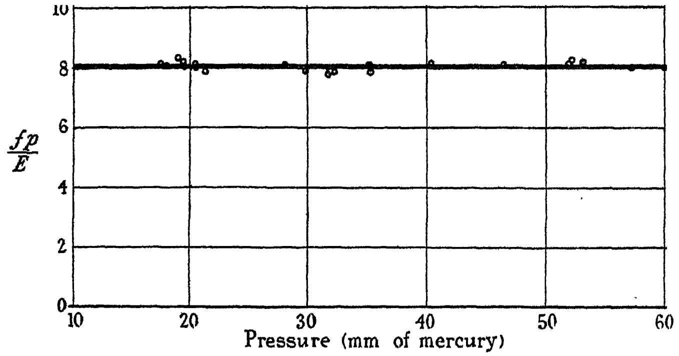

FIG. 4.

Determination of Absolute Values of Mobility.

The form of apparatus used in the experiments described above was not suitable for absolute determinations of mobility. At the peak frequency, the ions travel from the grid B to the grid D in one period of the alternating field, and since the grid C alternates in potential the field in which they move at any moment is only known approximately. This objection is removed in a second form of the apparatus specially designed for absolute measurements.

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* Huxley, 'Phil. Mag.,' vol. 5, p. 721 (1928).

In this apparatus it was arranged that the distance BC could be varied. Readings were then taken of the electrometer current for different distances when the frequency and the main *field* were both kept constant. The current will then be a maximum when the distance BD is covered in an integral number of periods of the alternating field.

Consequently, when the current is plotted with the distance BC a series of peaks will be obtained, the distance between two consecutive peaks being the distance travelled by the ion in one period. In this way the end effect due to the alternating potential on the shutter is entirely eliminated.

The details of the experimental tube are shown in fig. 5. The guard rings are increased in number to 16 and their diameter to 4 cm. The shutter AB is attached to a pyrex tube which can slide telescopically inside another glass tube which is fixed to the rest of the apparatus. Enclosed in this movable tube are also the electrodes for the glow discharge ; the diameter of this tube and of the shutter is such that they can pass through the central holes of the guard rings with a small clearance. The source of the ions was a short tungsten filament P which could be raised if required to incandescence. While this was done during the bake out, it was not found necessary to use it hot in order to maintain a steady glow discharge. The two leads from it were used to form a fairly rigid connection with a small glass tube T in which an iron cylinder W was hermetically sealed. The slide could thus be moved by means of an electromagnet outside the vessel, so that the distance B—C had any desired value. The potentials to the four electrodes carried by the slide were applied through five flexible tungsten springs, of which four are shown in the figure.

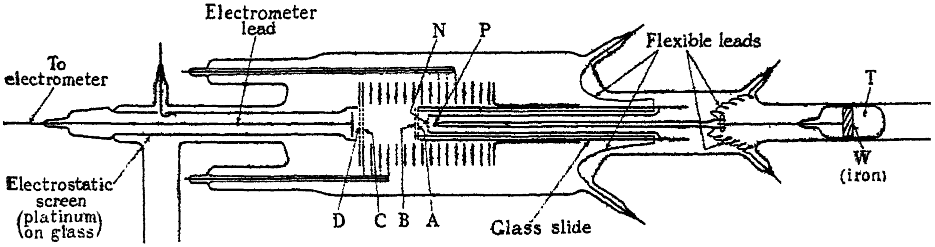

FIG. 5.

Results.

Three typical curves showing the variation of the electrometer current with distance, keeping the field between B and C constant, are shown in fig. 6. Despite the variations in field, pressure and frequency the values of the mobility calculated from these three curves and reduced to a pressure of 760 mm. of mercury are sensibly the same. It will be seen that though there are small fluctuations in the height of the peaks due to slight changes in the glow discharge the effects of diffusion are small. Had this not been so, the peaks would have become progressively lower and more diffuse as the distance increased. That the peaks are sensibly equidistant in any curve is shown in

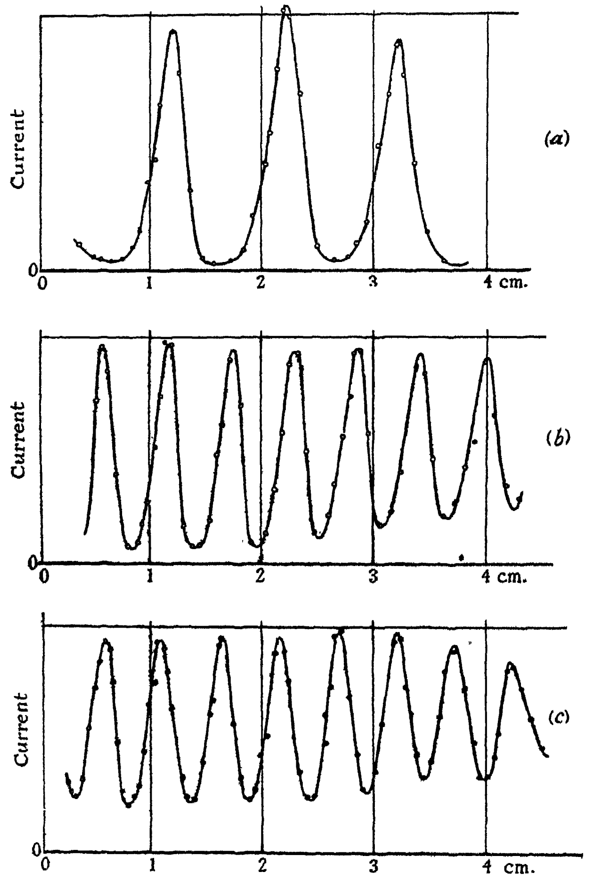

FIG. 6.—(*a*) Helium at 38·7 mm. Field, 31·7 volt/cm. Frequency, 13320. Mobility, 21·4.
(*b*) Helium at 38·6 mm. Field, 31·7. Frequency, 23950. Mobility, 21·7.
(*c*) Helium at 58·6 mm. Field, 20·0. Frequency, 10610. Mobility, 21·5.

the following table, where the results of individual experiments in pure helium are analysed.

Table.

p (mm.).	E (volts/cm.).	f (cycles/sec.).	Distance between peaks (cm.).					Mobility cm./sec./volt/cm.
			1st to 5th.	2nd to 6th.	3rd to 7th.	4th to 8th.	Mean.	
37·5	30·98	24190	2·26	2·25	2·20	2·19	0·556	21·5
38·6	31·66	23950	2·30	2·23	2·24	—	0·564	21·7
42·2	30·98	22520	2·10	2·09	2·08	2·10	0·522	21·0
58·6	19·96	10610	2·13	2·12	2·06	2·07	0·524	21·5
60·4	20·29	10610	2·07	2·04	2·05	2·02	0·511	21·3
38·7	31·66	13320	3 peaks				1·00	21·4
								Mean 21·4

The accuracy of the value of mobility obtained depends upon the measurement of the following quantities (*a*) changes in the distance between the shutters; (*b*) pressure on a U-tube mercury gauge; (*c*) voltage to produce the main field using a standard voltmeter; (*d*) frequency obtained with high accuracy from a standard tuning fork. The mean value of 21·4 cm./sec./volt/cm. for positive helium ions moving in helium gas may be claimed to be accurate to the order of 1 per cent.

No theoretical calculation of the mobility of a charged helium atom in helium gas has yet been made with the aid of the quantum mechanics. Hassé deduced the value 26·0 from Langevin's theory, and in a recent paper he and Cook have shown that this value must be too high, since exchange processes are neglected in obtaining it. On the arbitrary assumption that the probability of electron transfer at any gas-kinetic collision is one-half,* they show that the theory gives the value 21·0 if the atoms and ions are regarded as elastic spheres and 19·7 using the Sutherland model.

An accurate calculation of mobility can, however, only be carried out from a knowledge of the forces between a helium ion and a helium atom. Too much significance must not therefore be attached to the good agreement between the mean of the above values (20·35) and the experimental value (21·4). At the same time it justifies the view that in pure helium the normal positive helium ion is a charged atom and that the lower values ranging from 5·09 to 6·7 obtained by some earlier investigators were the result of the clustering of impurity molecules around the ion.

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* 'Phil. Mag.,' vol. 12, p. 554 (1931).

Finally, it may be pointed out that this method should be valuable in making measurements on the probability of electron transfer. Suppose that the apparatus is filled with an inert gas A containing a small percentage of another inert gas B of lower ionisation potential. If, throughout the path of the ions across the main field, capture of electrons by the ions of A from the atoms of B takes place, then, in the general case, the current-distance curve obtained will be the resultant of two sets of peaks, one of decreasing and the other of increasing amplitude with distance. The high resolving power of the apparatus should enable the resultant curve to be analysed if the mobilities of the two types of ions differ by more than 5 per cent. Since the gas A can be at high pressure and the percentage of the gas B added can be, say, 1 per cent. without appreciably affecting the mobility of either ion, the number of collisions of the ions of A with the atoms of B can be made very great indeed. We should therefore be able to detect cases of transfer which are relatively improbable; in this respect the method should have a great advantage over positive ray methods. Experiments with this end in view are now being undertaken.

We are indebted to the Department of Scientific and Industrial Research for a maintenance grant in aid of the investigation, and to the Colston Research Society of the University of Bristol for the gift of some of the apparatus.

Summary.

The mobility of positive ions of helium in pure helium has been determined by an accurate method and found to be 21·4 cm./sec./volt/cm. at 760 mm. of mercury and 20° C. The speed of the ions is proportional to E/p, where E is the field in volts per centimetre and p is the pressure in millimetres of mercury over a range of E/p from 0·3 to 4·2.

The Quantum Mechanics of Electrolysis.

By R. W. Gurney, Ph.D., Trinity Hall, Cambridge.

(Communicated by Lord Rutherford, O.M., F.R.S.—Received July 23, 1931.)

As quantum mechanics endows particles with entirely new properties, it enables us to deal with problems which have remained unsolved for many years. In electrolysis we have been unable to visualise the physical processes which underlie some of the most elementary phenomena. Thermodynamics gives a consistent account of them, independent of any mechanism; but when we try to unravel the actual processes their complexity is baffling. Quantum mechanics provides a new line of attack. One conception we find for our purpose particularly valuable—the idea that there always exists a finite probability of a particle making a spontaneous transition between any two states of equal energy.

In the Sommerfeld theory of metals the valence electrons of the metallic atoms are all free electrons, so that we may regard the atoms of the metallic crystal as ions. Applying this to the anode of a copper voltameter, for example, we may say that when a current is passed, ions from the crystal lattice are leaving the surface of the electrode and slipping away into solution. The same is true of reversible gas electrodes. In great contrast to this are the processes at the electrodes of a cell where an acid is being decomposed by electrolysis. Here ions from the electrolyte are being neutralised by actual capture and loss of electrons, evolving neutral oxygen and hydrogen. Thus the phenomena of electrolysis fall into two classes, both of which may be treated by quantum mechanics. In the electrolysis of acids we encounter the complicated phenomena of "overpotential," which provides an elaborate test for our theory; for this reason we shall be dealing in this paper with only these irreversible processes.

§ 1. *Irreversible Electrolytic Phenomena.*

Suppose that we have two plane platinum electrodes of unit area dipping into a dilute acid, such as sulphuric acid, which has been carefully freed from dissolved oxygen. If we apply between these electrodes an e.m.f. of, say, 1·2 volts, the value of the steady current which will flow is only 10^{-6} amps. If we now increase the potential difference between the plates by steps to 1·4, 1·6 and 1·8 volts, the value of the steady current rises to about 10^{-5},

10^{-4}, and 10^{-3} amps. respectively. Since the resistance of the electrolyte is quite low, the ohmic drop of potential in the solution must at these low currents be very small. The whole drop of potential occurs at or near the two electrode-liquid surfaces of contact; we will denote these two "electrode-potentials" at the anode and cathode by V_a and $-V_c$ respectively. When we increase the applied e.m.f. the anode becomes more positive with respect to the electrolyte by a definite amount, and the cathode more negative with respect to the electrolyte by a definite amount. We do not know whether at the lowest currents the potential difference is divided equally between the two electrode-potentials, *i.e.*, whether $V_a = V_c$. But we do know that, when the electrodes are similar and have equal area, any increment in the applied e.m.f. is shared equally between them, *i.e.*, $\Delta V_a = -\Delta V_c$. If, instead of increasing the applied e.m.f., we raise the temperature at constant potential difference, the current increases exponentially, as before. For a rise of temperature of about 40° C. the current is increased by a factor of 10. The details of the effects collected from Bowden's papers,* are as follows:—

(*a*) For electrodes of different areas there is a relation between increment of current density and increment of electrode-potential which is independent of the area of the electrode.

(*b*) This relation is given by $d(\log i) = C\,dV$, where C is a constant.

(*c*) Over the small range of temperature which can be investigated the variation of the current density for a particular value of V is given by $d(\log i) = B\,dT$, where T is the absolute temperature.

(*d*) The parameter C decreases with increasing temperature; in fact, it is inversely proportional to the absolute temperature. The relation is $d(\log i)/dV = A/T$, with $A = 5600$ if V is reckoned in volts, and $A = 1 \cdot 7 \times 10^6$, if V is expressed in electrostatic units.

(*e*) Although it is oxygen which is being discharged at the anode and hydrogen at the cathode, the same value of A, $1 \cdot 7 \times 10^6$, is found for both anodes and cathodes of platinum, within the experimental error.

(*f*) For cathodes of silver, mercury, nickel, and platinum, the same value, $1 \cdot 7 \times 10^6$, is found within the experimental error.

(*g*) The parameter B decreases with increasing V. For both anode and cathode its values are mainly between 0·05 and 0·06 over the range 0° to 80° C., at these current densities.

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* Bowden, 'Proc. Roy. Soc.,' vol. 125, p. 446 (1929); and vol. 126, p. 107 (1929).

From the theory given in this paper numerical agreement is obtained on all these points.

Although the problem is more than 40 years old, and experimental papers on the subject are poured out every year, very little systematic work has been done at sufficiently low current densities to reveal the elementary processes. In 1899 the name Ueberspannung, or Overpotential, was given by Caspari* to this class of phenomena. In 1905 the linear relation between log i and V was found by Tafel.† The other relations given above are due to Bowden, who has made a comprehensive investigation by the passage of extremely small quantities of electricity.‡ To account for his results Bowden tentatively put forward a chemical theory of overpotential in which the phenomena are treated as a surface reaction due to activated dipoles. He supposed that when a small current is passed, a single layer of dipoles is deposited on each metal surface, consisting of hydrogen in some form at the cathode, and of oxygen in some form at the anode, the potential difference across the interface being controlled by the number and electric moment of these dipoles. Further changes in the electrode-potential were attributed to an increased deformation of the adsorbed dipoles, with consequent increase in electric moment. When electrolysis is taking place, it is supposed that the evaporation or collapse of these adsorbed dipoles is occurring continuously. Bowden assumed that the energy of the dipoles is distributed according to the Boltzmann law, and that only those dipoles which possess energy greater than W can leave the surface. " Energy of activation " can be supplied to the dipoles by raising the temperature or by increasing the electrical potential across the layer, which causes a further deformation of the dipoles with consequent increase in their potential energy, by an amount proportional to V. The total energy necessary is then given by $W = w - \alpha V$, where w and α are constants. The number of dipoles which possess sufficient energy to leave the surface will now be given by $N = N_0 \exp\{-(w - \alpha V)/RT\}$, which leads to $d(\log i)/dV = \alpha/RT$, similar to the observed relation.

In the present paper attention is focussed on the neutralisation of the electrolytic ions arriving at the electrodes. This is treated by quantum mechanics, and it is shown that we are led to just the effects given in the above list, without making any *ad hoc* assumptions.

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* Caspari, 'Z. Phys. Chem.,' vol. 30, p. 89 (1899).

† Tafel, 'Z. Phys. Chem.,' vol. 50, p. 641 (1905).

‡ Bowden, *loc. cit.*; also Bowden and Rideal, 'Proc. Roy. Soc.,' A, vol. 120, p. 59 (1928) Bowden and O'Connor, *ibid.*, vol. 128, p. 317 (1930).

§ 2. *Application of Quantum Mechanics.*

The neutralisation of electrolytic ions will be more easily visualised if we first consider the neutralisation of a gaseous ion. When we say that the positive ions give up their charge to the electrode, we usually consider that they capture an electron by impact. But according to quantum mechanics no sort of contact is necessary, for an electron may make a spontaneous transition from the metal to a distant positive ion in the gas. What is more, to neighbouring ions these transitions take place so readily that positive ions cannot exist in the immediate neighbourhood of a metal except in special circumstances. Such neutralisation at a distance was first suggested by Compton and Van Voorhies* to account for certain experimental results obtained by them with gaseous ions. It has since been pointed out by Oliphant and Moon† that the process would be anticipated from quantum mechanics. The situation is illustrated in fig. 1, where is sketched the potential energy of an electron along a line perpendicular to the surface of the metal. Here MM represents the occupied electron levels in the metal. According to the Sommerfeld theory, the valence electrons obeying the Fermi-Dirac statistics are distributed over a range of about 7, 9 and 12 volts in di-, tri-, and quadri-valent metals, respectively. The work-function of the metal, ϕ, is the negative energy of the highest occupied level with respect to the energy of an electron outside the metal. In fig. 1 is sketched also the Coulomb field and vacant level of a neighbouring ionised atom. Between the levels in the metal and those in the ion is a region forbidden by classical mechanics to electrons of these energies. If, however, the electrons in the metal are represented by a wave-function, this will not vanish at the surface of the metal, but will die away exponentially into the potential barrier. Since the number of electrons incident on unit area of the boundary from within is about 10^{30} per second, this penetration into the potential barrier is by no means negligible, but indicates a high probability of transition from

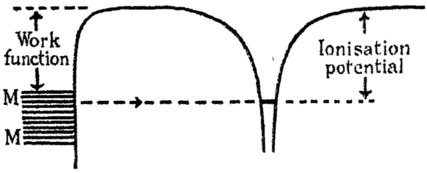

Fig. 1.

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* Compton and Van Voorhies, 'Proc. Nat. Acad. Sci.,' vol. 13, p. 336 (1927), and 'Phys. Rev.,' vol. 30, p. 318 (1927).

† Oliphant and Moon, 'Proc. Roy. Soc.,' vol. 127, p. 388 (1930).

the metal to a vacant level of equal energy in any neighbouring ion. The interaction matrix for such a transition has been worked out by Massey.[*] It appears that the chance of a positive ion remaining within a few molecular diameters of the metal for a millionth of a second without being neutralised is extremely small.

At first sight this effect appears inconsistent with the existence of an electrical double layer of positive ions on a negative metal surface, such as are known for cæsium on tungsten.[†] But since the above considerations only apply to electron-transitions between levels of equal energy, no transition can occur if the ionisation potential, $\mathfrak{J}$ of the ion (when neutralised) is less than the work-function of the metal, as is clear from fig. 1. It was in fact found that this condition must be satisfied.[†] The alkalies and heavier alkaline earths are the only elements whose ionisation potentials are less than 4 to 6 volts.

We have not yet considered the reverse transition from a negative ion, or neutral atom, to the metal. Evidently this transition is possible from an atom whose ionisation potential is less than ϕ; for in this case the electron can find for itself a vacant level in the metal above the occupied levels. Langmuir and Kingdon, in fact, found that neutral atoms of alkali metals, incident on a filament, were all scattered as positive ions, when ϕ was greater than the ionisation potential $\mathfrak{J}$. But from atoms whose levels are lower, an electron-transition to the metal is almost impossible, since practically all possible states in the metal of equal energy are already occupied.

We have so far been considering the simple case of a gaseous ion in field-free space. The situation is very different if the ion possesses potential energy of its own, due to the interaction of its charge with some other charge. If in this case an electron makes a transition from the metal to the ion, neutralising the ionic charge, this potential energy is annihilated. But, of course, these electron transitions may only take place subject to the conservation of energy. Hence it is essential that the electron-level in the metal from which the electron comes shall be higher or lower according as the ion has negative or positive potential energy (fig. 2).

These considerations indicate an important difference between ions in liquid solution, and ions in a gas. For electrolytic ions, owing to their interaction with adjacent water molecules, are all in a state of having lost energy—namely, the " heat of hydration," which has been given out. This negative potential energy of the ion itself, which we shall denote by W, and which usually amounts to several ε-volts per ion, must be replaced when the ion is neutralised, in order to conserve energy. It is no longer true that the necessary condition for neutralisation of positive and negative ions is that ϕ be less or greater than the ionisation potential $\mathfrak{J}$. But we can define a quantity, instead of $\mathfrak{J}$, for which this is true; we shall call this quantity the neutralisation potential and denote it by E. Then the necessary condition for the required electron transition to be possible is for a positive ion $E_+ > \phi$ and for a negative ion $E_- < \phi$, where

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[*] Massey, 'Proc. Camb. Phil. Soc.,' vol. 26, p. 386 (1930).

[†] Langmuir and Kingdon, 'Proc. Roy. Soc.,' vol. 107, p. 73 (1925).

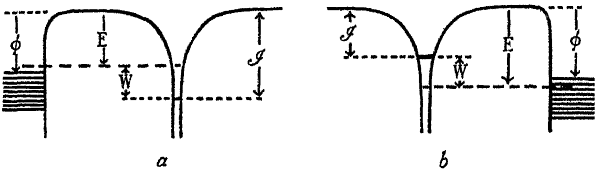

Fig. 2.—Showing the relations between W, $\mathfrak{J}$, and E for (*a*) positive ions, and (*b*) negative ions.

$$E_+ = \mathfrak{J}_+ - W_+ \qquad \text{and} \qquad E_- = \mathfrak{J}_- + W_-. \tag{1}$$

Fig. 2, *a* illustrates a case where transition to a positive ion would have taken place in a vacuum or gas, but is impossible in solution, because the required level is now an unoccupied level; similarly in fig. 2, *b*, the transition to the metal has become impossible because the required level is now an occupied level.

§ 3. *Electrode Potentials.*

It will now be clear that the presence of a rapid change of potential at the metal-liquid interface, *i.e.*, an electrode-potential such as we usually find, may well be the controlling factor in governing the neutralisation of ions. With regard to fig. 2, *a* and *b*, it is evident that in each case the electron-transition would become possible if the sign of the electrode-potential were such as to shift the level in the required direction. A moment's reflection shows that the sign of the electrode-potential which we find at cathodes is the sign which will promote the neutralisation of positive ions; while that which we find at anodes will promote the neutralisation of negative ions. In fact, the view which will be put forward in this paper is that the overpotential is not in this case due to an obstructive film of gas on the electrode, but, on the contrary, is an essential condition without which decomposition of the electrolyte cannot proceed. The effect of an electrode-potential V is to reduce the work-function at the cathode effectively to $\phi - V$, or to increase that at the anode effectively to $\phi + V$. Hence the conditions to be satisfied are now

$$E_+ > \phi - V_c \qquad E_- < \phi + V_a. \tag{2}$$

From the above discussion of neutralisation potentials it might be supposed that it would be possible at any rate to imagine an acid whose ionic levels were such that one could electrolyse it without the existence of electrode-potentials. A moment's consideration shows, however, that this is not so. For electrolysis to take place we need simultaneously $E_+ > \phi$ and $E_- < \phi$. But this implies $E_+ > E_-$, which is incompatible with ionic dissociation. The reason why electrolytes are dissociated into their ions, in the first place, is that the state of (ionisation + hydration) is a state of lower energy than the undissociated state. If the level occupied by the electron in the hydrated negative ion were not lower than the unoccupied level in the hydrated positive ion, electrons would immediately filter across from one to the other through the intervening potential barrier, until all the ions were neutralised. Thus in all highly dissociated electrolytes the neutralisation potentials of the ions are such that $E_+ < E_-$. And the necessary condition for decomposition by electrolysis can only be brought about by the presence of electrode-potentials. In § 4 we shall use this idea to predict the list of observed phenomena given above. But before we do this, we must make an excursion into electrostatics.

Consider an ion in a gas. In the neighbourhood of a metal surface the ion is attracted to the metal by the mirror-image force. The potential energy falls slowly as in fig. 3, *a*; at contact with the metal the force becomes suddenly repulsive, and the curve rises rapidly. At room temperature the thermal kinetic energy of the ion is about 1/25 volt. But under the attraction of the mirror image the ion will acquire a kinetic energy 10 times this normal value at a distance of 15 molecular diameters from the metal surface; while near the surface the kinetic energy will be more than 100 times its normal value. If the ion make an elastic impact on the metal, it will retrace its path and move off into the body of the gas with its original energy of 1/25 of a volt.

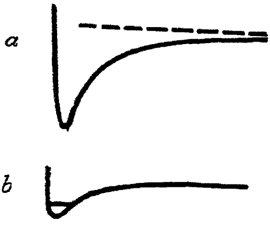

Fig. 3.

The ionisation potential of a hydrogen atom is nearly the same whether it happens to be dissolved in water or situated in a vacuum; that is to say, the forces between the proton and electron are nearly the same. At large distances, however, we know that in a medium of dielectric constant K the force between charges is 1/K of its value in a vacuum. Applying this to the mirror-image forces near an electrode, we see that at large distances from the surface the mirror-image force will be only 1/K of its value in a gas. But at a distance of one or two molecular diameters from a clean metal surface the effective factor 1/K tends towards unity. The dip in the potential energy curve will therefore be confined to a small layer next to the metal, fig. 3, *b*.

The condition of escape of the gaseous ion considered above was that it retained at least some of its original 1/25 volt of energy. If by colliding with a gas molecule it had given up more than 1/25 volt, it would have been unable to escape. This is what will happen to an electrolytic ion. Owing to the extremely small free path, the chance of an ion *not* making a collision while it has its abnormally high kinetic energy is very small. The ion will be trapped in the potential pocket, as in fig. 3, *b*.

These considerations apply equally to positive and negative ions. When therefore an electrically neutral metal surface is exposed to a dilute electrolyte, the ions of both signs which happen to be near the surface will be trapped. Water molecules still cover the greater part of the metal surface, but since each ion which approaches the surface is liable to be trapped, we shall have these water molecules being ousted by ions of both signs, until finally there are perhaps no water molecules left in contact with the metal except those water molecules which are bound to the ions by the hydration forces. All that this means is that in contact with the metal the concentration of the electrolyte will be much greater than in the body of the solution. But suppose next that at the moment when the metal was exposed to the electrolyte it was electrically positive with respect to the latter; in this case there is a tendency for more negative ions to be trapped than positive, while if the metal were negative an excess of positive ions would be trapped. The charge of these ions distributed over the surface will give rise to a potential difference V, which we can calculate from $N\varepsilon = CV$, where C is the capacity of the double layer formed by the surplus ions and their mirror images. The excess number of ions N required to give a potential difference of 1 volt will be

$$N = \frac{K}{4\pi d 300\varepsilon} \text{ per unit area.} \tag{3}$$

Writing $d = 2 \times 10^{-8}$ cm., and $K = 1$, we find $N = 3 \times 10^{13}$. As there may be more than 10^{15} ions per unit area in contact with the surface, it is clear that ions of one sign need be little in excess of ions of the other sign to give the observed electrode-potentials of one or two volts. The required excess is much smaller than the number of ions in one monomolecular layer, so that the change of potential can take place in one molecular diameter from the metal surface. At each electrode the number of positive and negative ions in contact with the metal will never differ by more than a few per cent. If the potential of the metal is raised by means of applied e.m.f., those ions of the same sign which have at the moment the highest thermal energies will be repelled, and their places in contact with the metal taken by ions of the other sign, which are being attracted.

When two such metal electrodes are joined by an external circuit, as in an electrolytic cell, the equilibrium of the layer of ions on one electrode is not independent of that of the layer on the other. Any change in the electrode-potential at one electrode sends an electric charge through the external circuit, which, arriving at the other electrode, will disturb the equilibrium of ions there. If N positive ions are replaced by negatives on the surface of one electrode, and simultaneously N negatives are replaced by positives on the surface of the other electrode, then 2N electrons will meanwhile flow through the external circuit, producing a transient current. Neutralisation of ions plays no part in these transient currents. Bowden and Rideal measured the charge $N\varepsilon$ passing through the external circuit during the establishment of a measured over-potential. At a smooth mercury cathode they found $N\varepsilon = 3 \cdot 6 \times 10^{13}\varepsilon$ per volt rise in V. The value calculated above from (3) is in excellent agreement with this.

§ 4. *Outline of the Theory.*

In contemporary physics there are two ways of regarding the hydration of ions. One prefers to leave the state of hydration indefinite,* while the other postulates the formation of definite molecular ions, so that, for example, $(H_2O \,.\, H)^+$ and $(H_2O \,.\, OH)^-$ are formed by the hydration of H^+ and OH^- respectively.† The two views are not mutually exclusive ; the former draws its conclusions from general considerations, but of recent years there is considerable support for the complex ion theory. In § 2 we have spoken of the hydration energy W as if it had one definite value for all the ions of one kind ; but in neither theory is this true. In the general form of the theory the mean hydration energy is obtained from the virial by summing over all possible configurations. In the complex ion theory the molecular ion will have a large number of vibration levels in which the ions will be distributed according to Boltzmann's law. (We shall suppose that these vibration-rotation levels are sufficiently close together and sufficiently blurred by the interaction with adjacent molecules to be treated as forming an almost continuous spectrum of levels.) It is clear that the single level of fig. 2, *a* or 2, *b*, and the single value of the neutralisation potential must be replaced by a wide band of levels, labelled in excellent agreement $E_0{}^+$ and $E_0{}^-$ in fig. 4.

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* Born, 'Ver. D. Phys. Ges.,' vol. 21, p. 13 (1919) ; Fajans, *ibid.*, p. 709.

† Hund, 'Z. Physik,' vol. 32, p. 13 (1925) ; Brönsted, 'J. Phys. Chem.,' vol. 30, p. 777 (1926) ; Hunt and Briscoe, 'J. Phys. Chem.,' vol. 33, p. 1509 (1929) ; Goldschmidt and Mathiesen, 'Z. Phys. Chem.,' vol. 121, p. 156 (1926) ; Kendall and Gross, 'J. Amer. Chem. Soc.,' vol. 43, p. 1424 (1921).

The hydration energy W_0 of those molecular ions which are in their lowest vibration-rotation level is equal to the full dissociation potential of the molecular ion. But for a molecular ion in its *n*th vibration-rotation level $W_n < W_0$, since the work required to dissociate the ion is less by an amount equal to the excess vibration-rotation energy. Since for a positive ion $E = \mathfrak{J}_+ - W$, it is clear that $E_n > E_0$, and that $N_+ (E)$, the number of positive ions with neutralisation potential between E and $E + dE$ will be given by the Boltzmann law, $N (E) = N_0 e^{(E_0 - E/kT)}$. On the other hand, for negative ions the neutralisation potential is given by $E = \mathfrak{J} + W$; hence $E_n < E_0$, and $N_- (E)$ will be an inverted Boltzmann distribution. These two distributions are labelled $E_0{}^+$ and $E_0{}^-$ in fig. 4, which will be explained in detail later.

We can now return to the consideration of electrode-potentials which was begun in § 3. It was there pointed out that the essential condition for a large current flowing is that there should be a large overlapping between the ionic and metallic electron-levels between which transitions can take place. We find now that the conditions which must be satisfied for neutralisation to take place are for positive ions at the cathode

$$E_n > \phi - V_c, \tag{4}$$

and for negative ions at the anode

$$E_n < \phi + V_a, \tag{5}$$

and these cannot be simultaneously satisfied with $V_c = V_a = 0$. The number of ions for which (4) is satisfied at the cathode is given by

$$\int_{\phi - V_c}^{\infty} N_+ (E) \, . \, dE.$$

And if P(E) is the probability of an electron making a transition from the metal to an ion through a potential barrier of height E, the current flowing will be given by

$$\int_{\phi - V_c}^{\infty} N_+ (E) \, . \, P (E) \, . \, dE. \tag{6}$$

When a steady current is flowing, the number of electrons which are making transitions through the potential barrier from the cathode to the positive ions must be equal to the number of electrons making transitions from the negative ions to the anode. This integral must therefore be equal to the corresponding integral at the anode. Suppose now that we wish to pass a larger steady current through the cell; both of these integrals must obviously be increased. But at constant temperature N (E), P (E), and ϕ are already fully determined. Therefore to produce the necessary increment there remains only the possibility of change in V at each electrode. This is the explanation of the familiar fact that any increment in applied e.m.f. is almost entirely taken up in increasing the potential differences at both the metal-liquid interfaces. It is just this necessary change in V which shows itself as the overpotential which is automatically set up by the replacement of ions, as described in § 3. Turning next to variation with temperature at constant potential difference, we see that the exponential increase of N(E) will cause the current to rise exponentially with the absolute temperature, in agreement with observation. We shall show that the theory leads to numerical agreement with experiment.

§ 5. *Theory and Results.*

In the foregoing outline we have treated the familiar work function ϕ as if it had a precise meaning. It would be properly defined if the dividing line between occupied and unoccupied levels in the metal were sharp. At room temperature, however, this is far from true. In accordance with the Fermi-Dirac statistics the number of free metallic electrons with energies between w and $w + dw$ is given by

$$n(w) = \frac{A\sqrt{w}}{1 + \exp\{(w - w_1)/kT\}} \tag{7}$$

where A is a constant. As will appear later, at the low current densities with which we are dealing, levels for which w differs little from w_1 make a negligible contribution to the current. Outside a narrow range of energies ($w_1 \pm 0 \cdot 01$ ε-volt) we can replace (7) by

$$n(w) = A\sqrt{w} \,.\, e^{(w_1 - w)/kT}, \qquad w \geqslant w_1, \tag{8}$$

$$n(w) = A\sqrt{w}\,(1 - e^{(w - w_1)/kT}). \quad w \leqslant w_1. \tag{9}$$

This distribution is illustrated diagrammatically by the blackened area in the anode and cathode in fig. 4. Above w_1 the number of electrons falls off exponentially with the same Boltzmann factor as that of the ionic levels.

Making use of this distribution, the integral (6), representing the current flowing, must now be replaced by

$$\int_{E_0+}^{E_1-\epsilon V} n\,(E, V) \,.\, N_+\,(E) \,.\, P\,(E)\,, dE, \tag{10}$$

where E_1 is the value of E corresponding to w_1 when V is zero. The corresponding integral at the anode will be

$$\int_{E_1+\epsilon V}^{E_0-} \nu\,(E, V) \,.\, N_-\,(E) \,.\, P\,(E) \,.\, dE, \tag{11}$$

where ν (E, V) is the number of vacant levels in the metal, which falls off below w_1 exponentially with the same Boltzmann factor. The similarity of the phenomena at anode and cathode is due to this fact.

The correct limits of the integrals (10) and (11), and their physical significance will be understood from fig. 4, which is a developed form of fig. 2. Ordinates are energies, E being reckoned downwards from the top of the diagram; a rough scale of volts has been indicated. The figure consists of three strips, representing levels in the cathode, electrolyte and anode. It has already been explained that in the central strip the blackened areas represent N_+ (E) and N_- (E). In the cathode and anode the blackened areas represent *n* (E, V). The representation of the exponentials is, of course, merely schematic, since in reality they fall to 10^{-8} of their value in a range of half a volt.

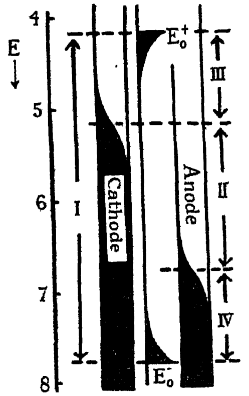

FIG. 4.—Abscissæ are N (E) in the central strip, and *n* (E, V) in the anode and cathode.

The range of energies marked I is a fixed property of the electrolyte; its boundaries are E_0^+ and E_0^-. We may take the potential of the electrolyte as the standard to which energies are referred; the cathode is displaced upwards by an amount V_c, while the anode is displaced downwards by an amount V_a. This displacement has brought an appreciable number of high energy electrons in the cathode to overlap the positive ion levels in region III, and at the same time has brought some appreciably unoccupied levels in the anode to overlap the negative ion levels in region IV. The range of energies marked II represents the magnitude of the applied e.m.f., which in this case is supposed to be sufficient to cause a detectable but not a large current to flow. The boundaries of region II are $E_1 - \varepsilon V_c$, and $E_1 + \varepsilon V_a$, the dotted lines having been drawn through the displaced metallic level w_1 of expressions (7), (8), (9). Region III is just the region of energies over which the integral (10) has to be taken ; its boundaries are E_0^+ and $E_1 - \varepsilon V_c$. From E_0^+ the number of vacant ionic levels falls off exponentially, but in the same region the number of metallic electrons is rising exponentially with the same Boltzmann factor, so that the product of the two exponential factors is everywhere the same. Thus the product $\{n(E) . N_+(E)\}$ is almost constant until we come near to the metallic electron-level of energy ($w_1 + 0 \cdot 01$ ε-volt) ; here the number of metallic electrons ceases to rise exponentially, so that the product falls very rapidly to a negligible value. We shall show later that the range of energies over which we have to integrate has for low-current densities a value about 1 ε-volt ; since this is large compared with 0·01 ε-volt, we may use the level corresponding to w_1 in the limit of the integral (10). Region IV is for the same reasons the range over which the integral (11) has to be taken. It will be understood from the diagram how any increase of temperature, or any small increase in the applied e.m.f., will cause the value of the product $\{n(E) . N(E)\}$ to rise exponentially. In so far as the metallic electrons are concerned, the rise of current with temperature takes place for the same reason as in the thermionic effect ; here, however, the ionic levels co-operate.

Let $N(E, x)$ be the number of ions per unit area at a distance x from the metal, having neutralisation potential E. When a steady current is flowing this distribution will, apart from thermal agitation, be steady. In an interval of time dt in any slab of the solution a certain number of ions will be neutralised, and their places taken by ions flowing in. Thus the total current density is given by

$$\iint n(E, V) . N(E, x) . P(E, x) . dE . dx.$$

To investigate orders of magnitude we shall take $P(E, x)$ to be the probability of transition through a rectangular potential barrier of height E and width x, and we shall suppose that all the ions are being neutralised at the mean distance x'. The essential part of P (E) will then be the factor $\exp(-4\pi x'/h . \sqrt{2mE})$.* Thus each of the terms in the integral (10) contains an exponential factor ; and the integral is to be taken over a small range of E where the other factors are relatively constant in comparison with the rapid variation of these exponential factors ; retaining only the latter, we have that the integral (10), representing the current density, is proportional to

$$\int_{E_0}^{E_1 - \epsilon V} e^{(E - E_1 + \epsilon V)/kT} . e^{(E_0 - E)/kT} . e^{-4\pi x'/h . \sqrt{2mE}} . dE. \tag{12}$$

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* Gurney and Condon, ‘Phys. Rev.,’ vol. 33, p. 131 (1929).

On integrating, we find

$$\log i = \frac{E_0 - E_1 + \varepsilon V}{kT} + \log\{(ax'\sqrt{E_0} + 1)\, e^{-ax'\sqrt{E_0}} - (ax'\sqrt{E_1} - \varepsilon V + 1)\, e^{-ax'\sqrt{E_1 - \varepsilon V}}\} + \text{const.}$$

Hence

$$\frac{d(\log i)}{dV} = \frac{\varepsilon}{kT} + \frac{\varepsilon a^2 x'^2 \,.\, e^{-ax'\sqrt{E_1 - \varepsilon V}}}{(ax'\sqrt{E_0} + 1)\, e^{-ax'\sqrt{E_0}} - (ax'\sqrt{E_1 - \varepsilon V} + 1)\, e^{-ax'\sqrt{E_1 - \varepsilon V}}} \quad (13)$$

where $a = 4\pi\sqrt{2m}/h$, and the value of E_1 is the work-function ϕ of the electrode. For the anode we have an identical expression if we take the appropriate sign for V. The values of E_0^+ and E_0^- must be about 4 ε-volts, and 8 ε-volts, respectively. The value of x' must be about 5×10^{-8} cm. Substituting these values in (13), we find that the second term is small compared with the first. We are left then with the simple term ε/kT, which will apply to both anode and cathode, and will be independent of the nature of the metal. It will be recalled that the term found by experiment is α/T, where α has the same value at anode and cathode, and is independent of the nature of the metal.

In order to present a more complete theory, we have to introduce a modification into the idea of the neutralisation potential. The elementary point of view taken in § 2 was that the mutual potential energy of the ion and adjacent water molecules was before neutralisation negative and equal to —W, and after neutralisation was zero. This is not quite correct, for if neutralisation takes place with stationary nuclei, as in the Franck-Condon principle, the mutual

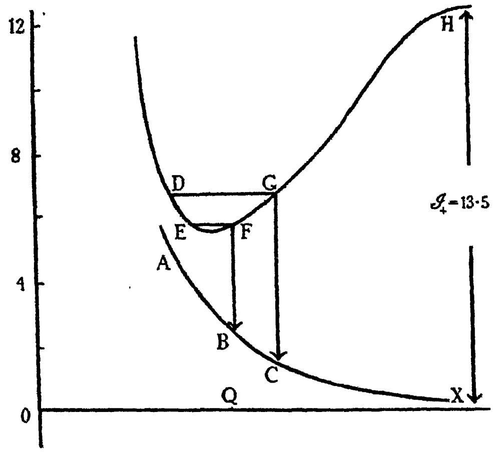

FIG. 5A.—Abscissæ are distances apart, the origin being the centre of gravity of the H_2O molecule.

potential energy immediately after neutralisation will be positive. This modification will be more easily made clear in terms of molecular ions. In 1925, investigating the molecular structure by the methods then available, Hund found a stable configuration for the $(H_3O)^+$ ion with a dissociation potential of about 8·3 ε-volts. Though this was done in the days before quantum mechanics, it may be of the right magnitude. Now $(H_3O)^+$ is one of those peculiar ions, like $H_3{}^+$, to which there is no corresponding neutral molecule. The symmetry properties of H_2O and neutral H are such that the force between them is repulsive at all distances, as in the antisymmetrical form of H_2. When neutralisation of $(H_3O)^+$ takes place, the components then fly apart evolving atomic hydrogen; the same is true of the complex negative ion, evolving oxygen. The potential energy of the neutral state of such ions must, therefore, be represented by a curve such as ABC, fig. 5A, similar to that which gives rise to the continuous spectrum of hydrogen. The curve for the stable vibrational levels of $(H_3O)^+$, represented by DFH will lie above the axis so that HX is the ionisation potential of the hydrogen atom, 13·5 ε-volts. The curve KMP, fig. 5B, for the negative complex ion will lie below the axis, so that PX is the ionisation potential of the unhydrated negative ion, which is usually only 2 to 4 ε-volts.* EF represents the lowest vibration-rotation level of $(H_3O)^+$ and the vertical distance of EF below H is the dissociation potential of the ion; the value. 8·3 ε-volts, deduced by Hund is in fair agreement with the hydration energy, From Born's theory† Fajans deduced a value of 11·5 ε-volts,‡ but in his calculation he used too small a value for the work function of the electrode; the correct value of the hydration energy must be nearer to 9 ε-volts.

Now it is clear that the transition representing neutralisation of an ion in its lowest vibration-rotation level is on this diagram FB for the positive ion, and MB′ for the negative ion; and this is in each case the neutralisation potential that must be used when we are considering the electron transition. From fig. 5 we see much more clearly than from fig. 2 how it comes about that for any hydrated positive ion the neutralisation potential, represented by FB, is less than ϕ for any electrode, in spite of the fact that $\mathfrak{I}$ is greater than ϕ; while for a negative ion the neutralisation potential, represented by MB′, is greater than ϕ, although $\mathfrak{I}$, represented by PX, is less than ϕ. In accordance with the Franck-Condon principle, BQ represents the positive mutual potential energy of the molecular components before they have moved apart. If R_n

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* Foote and Mohler, "Origin of Spectra," chap. 8.

† Born, *loc. cit.*

‡ Fajans, *loc. cit.*

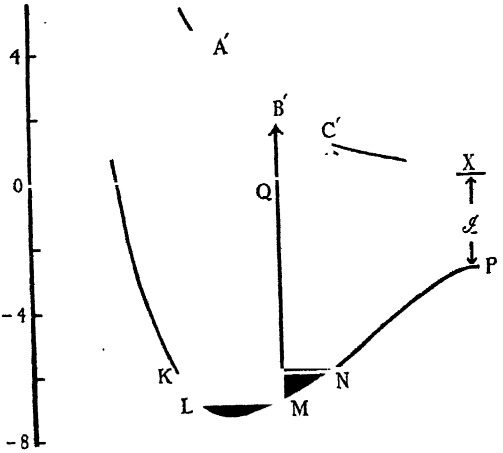

FIG. 5B.

is the value of this repulsive potential energy resulting from neutralisation of an ion in its nth vibration-rotation level, the correct expression for E_n is now,

$$\left.\begin{array}{ll}\text{for positive ions} & E_n = \mathfrak{J} - W_n - R_n \\ \text{and} & \\ \text{for negative ions} & E_n = \mathfrak{J} + W_n + R_n\end{array}\right\} \qquad (14)$$

Let DG be a vibration-rotation level about 1 ε-volt higher than EF ; it is only levels between EF and DG which concern us ; if U is the vibration-rotation energy, the distribution is given by $N(U) = e^{(U_0-U)/kT}$. From fig. 5 we see that (GC — FB), representing $(E - E_0)$ is greater than $(U - U_0)$; let $(E - E_0) = \gamma(U - U_0)$. Between E and E_0 we have the same number of levels as between U and U_0, but they are distributed over a larger range of energy. Therefore we have that $N(E) = N_0 e^{(E_0-E)/\gamma kT}$, where γ is greater than unity and to a first approximation constant. The value of γ depends on the relative slope of FG and BC ; if, for example, BC is sloping downwards at the same rate that FG is sloping upwards as in fig. 5, γ has the value 2. The same argument applies to the slope of MN and B′C′ for negative ions.

Since the term in (13) contributed by the potential barrier turned out to be small, we may treat P(E) as a constant. Instead of the integral (12) we have now

$$\int_{E_0}^{E_1-\epsilon V} e^{(E-E_1+\epsilon V)/kT} \,.\, e^{(E_0-E)/\gamma kT} \,.\, dE \qquad (15)$$

$$= e^{(E_0/\gamma+\epsilon V-E_1)/kT} \left\{e^{(E_1-\epsilon V)(1-1/\gamma)/kT} - e^{E_0(1-1/\gamma)kT}\right\} \,.\, \frac{\gamma kT}{\gamma - 1}. \qquad (16)$$

Of the two terms in the bracket the second has a value only 10^{-4} of that of the first when $\gamma > 1 \cdot 3$, as here. Retaining only the first term in the bracket, we find

$$\log i = \frac{E_0 - E_1 + \varepsilon V}{\gamma k T} + \log T + \text{constant.} \tag{17}$$

As our final result we obtain the two relations

$$\frac{d(\log i)}{dV} = \frac{\varepsilon}{\gamma k T} \qquad \gamma > 1, \tag{18}$$

$$\frac{d(\log i)}{dT} = \frac{E_1 - E_0 - \varepsilon V}{\gamma k T^2} + \frac{1}{T}. \tag{19}$$

Excellent agreement with experiment is found with a value $\gamma = 2$. It will be recalled that the observed relation is $d(\log i)/dV = A/T$, with $A = 1 \cdot 7 \times 10^6$. Since the value of k is $1 \cdot 37 \times 10^{-16}$ ergs, we have with $\gamma = 2$

$$\frac{\varepsilon}{\gamma k} = 1 \cdot 7 \times 10^6.$$

Over the small range of absolute temperature which is open to experiment it will be recalled that $d(\log i)/dT = B$, where the value of B decreases with increase in V. It will be seen that the numerator in (19) will be diminished by any increase in V, in agreement with observation. This numerator, $(\overline{E_1 - \varepsilon V} - E_0)$ will be recognised as the range of energies over which the integral (15) has been taken; throughout the investigation we have been supposing that this range of energies is about one ε-volt, or $1 \cdot 6 \times 10^{-12}$ ergs. It will be recalled that for both anode and cathode the observed values of B are between 0·05 and 0·06, for the temperature range 14° to 80° C. If we use the same value of γ as before, we shall have at 320° K., to compare with this,

$$\frac{1 \cdot 6 \times 10^{-12}}{2 \,.\, 1 \cdot 37\; 10^{-16} \,.\, 102400} = 0 \cdot 057.$$

§ 6. *Conclusion.*

The analysis of the problem has brought out clearly the important rôle played by the quantities E^+, E^-, E_0^+, E_0^-, which we have called the neutralisation potentials. In deriving these quantities we have used the only available vocabulary—that of molecular spectroscopy. The existence of definite molecules is not, however, a necessary assumption. Provided that the hydration energy is distributed according to the Boltzmann law, and has a relation corresponding to (14), indefinite molecular configurations would probably give the same results. Agreement with experiment has been obtained for all of the seven relations tabulated in § 1.

The writing of this paper would not have been undertaken but for the welcome instruction in the experimental data volunteered to me by Dr. F. P. Bowden, to whom I wish to express my thanks.

The Scattering of α-Particles by Light Elements.

By W. Riezler, Ph.D. (Munich).

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It is well known that the scattering of fast α-particles by light elements shows very remarkable deviations from the classical law of scattering deduced from the assumption that the nuclei behave as point charges, surrounded by a Coulomb field of force. The first anomalous effects of this kind were obtained in 1919 by Rutherford* in an investigation of the collisions of α-particles with hydrogen nuclei. Chadwick and Bieler† found in later experiments that the number of H-particles observed at small angles, which, seen from the centre of gravity of the colliding system, correspond to α-particles scattered through large angles, was for the fastest α-particles about 100 times larger than the number calculated on the assumption of Coulomb forces between the colliding particles. They suggested that this effect was due to an oblate spheroidal shape of the α-particle. This assumption also agreed with subsequent experiments by Rutherford and Chadwick‡ on the scattering of α-particles in helium. They found that for high velocities of the incident α-particles the number of particles scattered through 45° was about twenty times larger than expected. For smaller initial velocities and smaller angles this ratio became much less, for certain velocities only one-third.

The scattering of α-particles by the nuclei of other light elements has been observed only in two cases, those of magnesium and aluminium. The first investigations of this kind were those of Bieler.§ He found that the ratio of the observed scattering to that given by inverse square forces is close to unity for small angles, but diminishes as the angle increases, gradually for slow α-particles, more rapidly for the faster ones. Rutherford and Chadwick* extended these results and found that for large angles and fast α-particles the ratio of observed to calculated scattering after diminishing to a value of about one-third, began to increase again. In later (unpublished) experiments Chadwick found that the ratio increased in the case of fast α-particles scattered through very large angles to a value considerably higher than unity.† An explanation for the anomalous scattering shown by magnesium and aluminium has been advanced by Debye and Hardmeier‡ on general lines. If, as we suppose, the aluminium nucleus is a complex structure of positive and negative charges, this structure may be distorted or polarised in the field of the approaching α-particle. The polarisation gives rise to an attracting force on the α-particle, which varies inversely as the fifth power of the distance. Debye and Hardmeier showed that this hypothesis would account very fairly for the experimental results.

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* Rutherford, 'Phil. Mag.,' vol. 37, p. 537 (1919).

† Chadwick and Bieler, 'Phil. Mag.,' vol. 42, p. 923 (1921).

‡ Rutherford and Chadwick, 'Phil. Mag.,' vol. 4, p. 605 (1927).

§ Bieler, 'Proc. Roy. Soc., A,' vol. 105, p. 434 (1924).

We know now, however, that the laws of classical mechanics fail to give an adequate description of collisions when the de Broglie wave-length associated with the particles is not small compared with the distances of collision. In the collisions of α-particles with the nuclei of the lighter elements the distance of collision will be less than 10^{-12} cm. in the cases where the α-particles are scattered through a large angle, while the wave-length associated with a fast α-particle is about 5×10^{-13} cm. Thus we cannot expect classical mechanics to give a complete explanation of the anomalous scattering and we must rather consider the problem from the standpoint of the new mechanics.

In this paper some observations are described of the scattering of α-particles through large angles by beryllium, boron, carbon, and aluminium. The scattering shows large deviations from that predicted on the assumption of Coulomb forces between the particles. The deviations would probably be rather difficult to explain on classical mechanics, but, as will be seen later, the new mechanics predicts, at least qualitatively, exactly such results as were obtained.

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* Rutherford and Chadwick, 'Phil. Mag.,' vol. 50, p. 889 (1925).

† Rutherford, Chadwick and Ellis, "Radiations from Radio-active Substances," p. 269, Cambridge (1930).

‡ Debye und Hardmeier, 'Phys. Z.,' vol. 27, p. 196 (1926).

Apparatus.

The experimental arrangement will be clear from the diagram (fig. 1) and need not be described in detail. The source of α-particles was at P, the scattering element was placed at FF, and the particles scattered from the annular ring AA were counted on a zinc sulphide screen Z. The whole apparatus was contained in a large aluminium box, which was evacuated during the experiments. The source of α-particles was radium (B + C) deposited on the face of a platinum disk of 2·8 mm. diameter. This disk was fixed in a small brass box B, which could be evacuated independently of the main apparatus. Its opening O was closed by a thin sheet of mica. The scattering of α-particles of different ranges was examined by adjusting the thickness of this sheet of mica. A graphite shutter G could be rotated in front of the opening O so as to cut off entirely the α-particles from the source. In this way any contamination of the apparatus could be detected, and allowed for, if necessary.

Around the source holder B was placed a circular diaphragm D, through

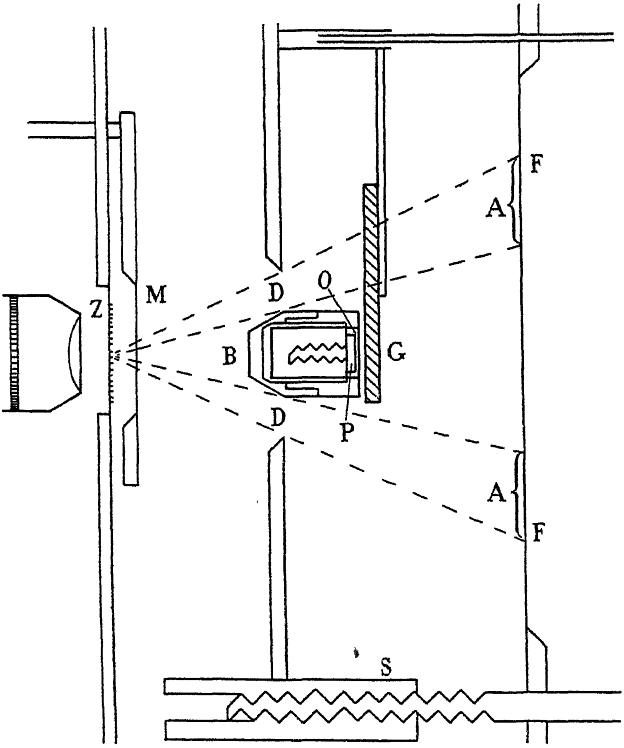

Fig. 1.

which only those particles which were scattered from the annular ring AA of the scattering foil FF could reach the zinc sulphide screen. In this way the scattering which was observed corresponded to a fairly narrow range of angle. The angular range could be changed during the course of an experiment by moving the source and diaphragm together on a slide S. The maximum mean angle of scattering observed in these experiments was 160°, the minimum angle 127°. For the large angles the range of angle was small, about ± 7° at 160°, including the variations due to the size of the source and of the zinc sulphide screen; the angular range was rather greater for the smaller angles, about ± 15° at 127°.

The scintillations produced on the zinc sulphide screen Z were observed through a microscope of large numerical aperture. The diameter of the visual field was 3 mm. A rotating screen M served to bring sheets of mica of different thicknesses in front of the zinc sulphide screen. By this means the range of the scattered particles could be determined. For experiments of the kind described here the scintillation method of detecting α-particles is much simpler and at present more certain than the electrical method. In the arrangement adopted in these experiments the source of α-particles, which is at the same time a source of β and γ radiation, was very close to the zinc sulphide screen. If an electrical method had been used, the ionisation chamber would have been exposed to strong β and γ radiations. A further disadvantage of the electrical method in these experiments arises from the fact that the ionisation chamber must contain gas and therefore be separated from the scattering chamber; thus an absorbing screen would be introduced in the path of the scattered particles, which already have a very small range owing to the fact that they have been scattered through large angles from a light element.

Of the light elements investigated, only aluminium could be obtained in the form of a thin foil. The other elements—beryllium, boron and carbon—were used in the form of thick layers. The disadvantage of a thick layer is, however, not so great as would appear at first sight. For these very light elements the ranges of the α-particles scattered through large angles are so small that the efficient thickness of the material, *i.e.*, the maximum depth from which the scattered α-particles can return to the surface, is of the same order of magnitude as the thickness of aluminium foil which was used. As an example, we may take the case of the scattering of α-particles of an incident range of 7 cm. by the heaviest of these elements, carbon. The range of the α-particle after scattering through 150° is only 1·0 cm.; thus the effective thickness of the carbon for scattering under these conditions is roughly that equivalent in stopping power to 1 cm. of air. For any given element the effective thickness depends on the scattering angle and on the range of the incident α-particles, and must therefore be calculated for each separate case.

Since the particles which are scattered to the zinc sulphide screen come from different depths in the scattering material they will have all ranges from zero up to a certain maximum defined by the conditions of each particular experiment. It is clear that some of the scintillations produced by such a beam of α-particles will not be counted. It is difficult to make an exact estimate of the fraction of the scattered particles which are missed in this way, and no allowance for this effect has been made in the observations recorded later in this paper. It must therefore be borne in mind that the true amount of scattering from a thick layer must on this account be somewhat greater than that actually observed. Calculations based on the energy distribution of the scattered particles and the data of Chariton and Lea* on the visibility of scintillations show that the fraction of particles missed was not greater than 15 per cent., even in the most unfavourable case.

The geometrical conditions of the experimental arrangement are such that it was not feasible to calculate accurately the scattering to be expected, under given conditions, on the assumption of inverse square forces. This was therefore deduced from observations of the scattering due to a thin gold foil under the experimental conditions. It is known that the scattering by gold follows exactly the Rutherford law.† From these measurements with a gold foil, the amount of scattering to be expected on the usual theory was calculated for the elements under investigation, with due regard to the motion of the nucleus in these cases.

Results.

Aluminium.—The scattering material was a foil of aluminium of thickness equivalent in stopping power for α-particles to 5 mm. of air. Observations were made with incident α-particles of one range only, viz., 6·8 cm. The scattered α-particles were found to have about the range to be expected if energy and momentum are conserved in the collisions. Some scintillations were observed when the absorption introduced at M (fig. 1) was greater than corresponded to the maximum range of the scattered α-particles. These were attributed to H-particles arising from disintegration collisions. Assuming that these H-particles were emitted equally in all directions, it was deduced that the total number emitted from the aluminium of 5 mm. stopping power was about 5 for 10^6 incident α-particles.

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* Chariton and Lea, 'Proc. Roy. Soc.,' A, vol. 122, p. 304 (1929).

† Rutherford and Chadwick, 'Phil. Mag.,' vol. 50, p. 889 (1925).

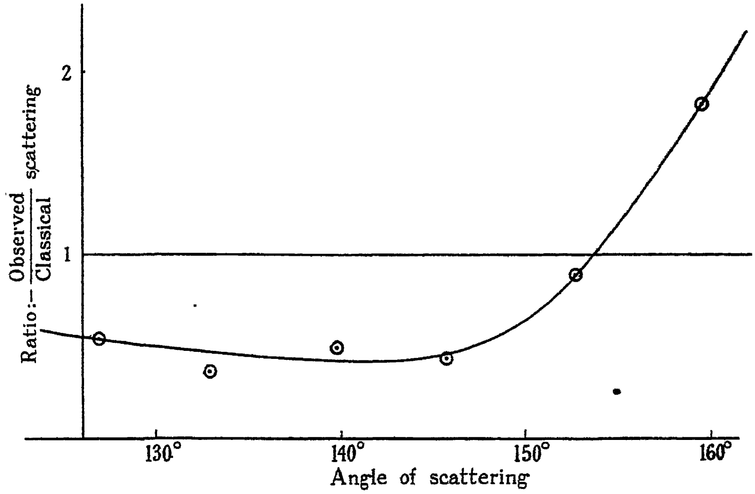

Fig. 2.

The observations made with aluminium are recorded in Table I.

Table I.—Scattering by Aluminium of α-particles of 6·5 cm. initial range.

Scattering angle.	Number of scattered particles per millicurie RaC′ for Al foil of 1 mm. S.P.		
—	Inverse square law.	Observed.	Ratio.
127°	0·650	0·368	0·57
133°	0·483	0·187	0·39
140°	0·356	0·184	0·52
146°	0·300	0·135	0·45
153°	0·273	0·246	0·90
160°	0·232	0·423	1·82

The results are shown graphically in fig. 2, in which the ordinates are the ratio of the observed scattering to that calculated on the assumption of Coulomb forces. It will be noticed that this ratio decreases with increasing angle of scattering, reaches a minimum at about 145°, and then rises again very rapidly to a value of about 2 for a scattering angle of 160°.

Carbon.

In these experiments the scattering material was a thick sheet of Acheson graphite. As was pointed out previously, the thickness effective in scattering depends on the initial range of the incident α-particles and on the scattering angle. For a scattering angle of 160° the effective thickness was that equivalent to a stopping power equal to 10·6 per cent. of the initial range of the α-particles. No particles were observed with ranges greater than those of the reflected α-particles.

Using incident α-particles of 6·8 cm. range, the angular distribution of the scattered particles was observed from 127° to 160°. About 250 particles were counted for each value of the scattering angle. The results are given in Table II.

Table II.—Angular Distribution of Scattering from Carbon for α-particles of 6·8 cm. initial range.

Angle.	Number of scattered particles.		
	Inverse square law.	Observed.	Ratio.
127°	1·75	1·92	1·10
133°	1·24	2·27	1·83
140°	0·87	3·15	3·62
146°	0·68	3·67	5·40
153°	0·53	4·13	7·8
160°	0·455	5·20	11·5

It will be seen that at 127° the amount of scattering is about that expected on Coulomb forces, while at 160° the observed scattering is about ten times as large. The results are also shown graphically in fig. 5, where the abscissæ are not the observed angles of scattering but the angles reduced to the centre of gravity (see note to fig. 5).

The variation of scattering with the velocity of the incident α-particles was also examined. The geometrical conditions were kept fixed to correspond to a mean angle of scattering of 160°, and the range of the incident particles was varied by using sheets of mica of convenient thickness over the opening O in front of the source (fig. 1). Since the incident particles pass through this mica sheet at different angles they reach the scattering screen with different ranges. The spread of range of the incident particles in each experiment is shown in the first column of Table III, which contains the experimental results.

Table III.—Scattering from Carbon through 160°. Number of Scattered Particles.

Initial range of α-particle.	Inverse square law.	Observed.	Ratio.
2·3–2·8	0·595	1·8	3·0
2·7–3·2	0·57	3·8	6·7
3·3–3·9	0·54	7·3	13·5
3·8–4·5	0·52	8·0	15·3
4·5–5·3	0·49	6·3	12·8
5·0–5·9	0·48	6·5	13·5
5·8–6·8	0·455	5·2	11·5

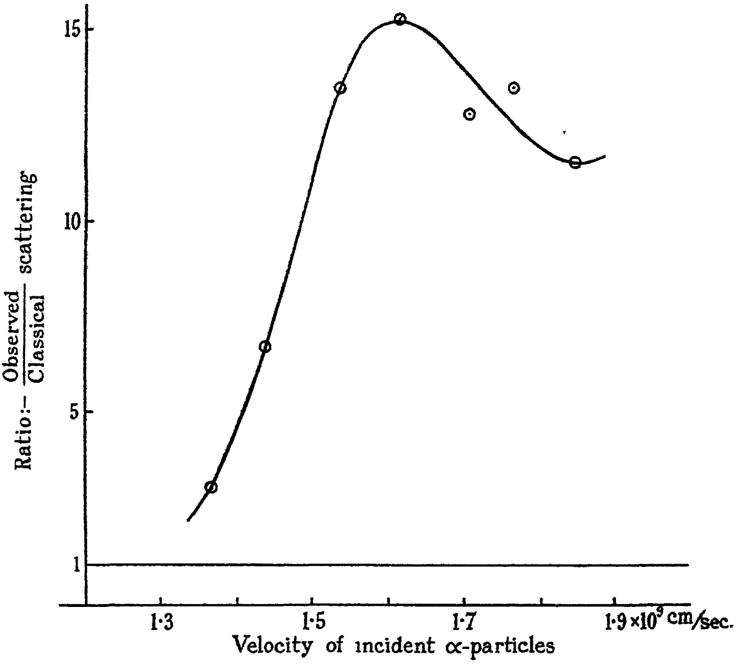

Fig. 3.

In each experiment about 300 to 400 scattered particles were counted. It will be seen (fig. 3) that the ratio of observed to classical scattering increases rapidly as the velocity of the incident α-particles is increased, reaches a flat maximum for a velocity of $1 \cdot 6 \times 10^9$ cm./sec., corresponding to an incident range of 4 cm., and then decreases slightly. Unpublished results of Chadwick obtained with incident α-particles of ThC′ indicate that the scattering rises again very rapidly as the velocity of the α-particle is increased beyond $1 \cdot 9 \times 10^9$ cm./sec.

Boron.

The scattering screen was a layer of pure amorphous boron (Kahlbaum) on a backing plate of graphite. The boron was finely powdered and was fixed to the graphite by means of amyl acetate.

Scintillations were observed on the ZnS screen when the absorption in the path of the scattered particles was greater than 1·6 cm. of air, which was more than sufficient to stop the scattered α-particles. These were presumably due to H-particles arising from the disintegration of boron. The number of these protons was roughly measured in each experiment and due allowance was made in estimating the number of scattered α-particles. It may be of interest to record that the number of protons observed varied rapidly with the range of the incident α-particles. Assuming that the disintegration protons are emitted equally in all directions, the observed numbers corresponded to about 15 disintegrating collisions for 10^6 incident α-particles of 6·8 cm. range, about 3 in 10^6 for incident α-particles of 5·5 cm. range, and about 1 in 10^6 for α-particles of 4·5 cm. range.

As with carbon, two series of observations were made. In the first, the angular distribution of the scattered particles between 127° and 160° was investigated, using incident α-particles of range 6·8 cm. The results are given in Table IV and in fig. 5.

Table IV.—Angular Distribution of Scattering from Boron for α-particles of 6·8 cm. initial range.

Angle.	Number of scattered particles.		
	Inverse square law.	Observed.	Ratio.
127°	1·04	2·55	2·45
133°	0·725	3·05	4·2
140°	0·485	2·7	5·6
146°	0·38	2·95	7·8
153°	0·295	3·3	11·2
160°	0·25	6·2	24·8

The ratio of observed to classical scattering changes from 2 at the smallest angle 127° to almost 25 at an angle of 160°. As we would expect, the deviation from classical scattering is even more marked with boron than with carbon.

In the second series of observations the scattering angle was kept fixed (160°) and the variation of scattering was examined as the velocity of the incident α-particles was changed. The results of this series are given in Table V and fig. 4.

Table V.—Scattering from Boron through 160°. Number of Scattered Particles.

Initial range of α-particle.	Inverse square law.	Observed.	Ratio.
2·4–2·8	0·34	0·83	2·4
2·8–3·2	0·32	1·42	4·4
3·4–3·9	0·305	1·98	6·5
3·9–4·5	0·29	2·1	7·2
4·6–5·3	0·275	2·45	8·9
5·2–5·9	0·27	5·0	18·5
6·0–6·8	0·25	6·2	24·8

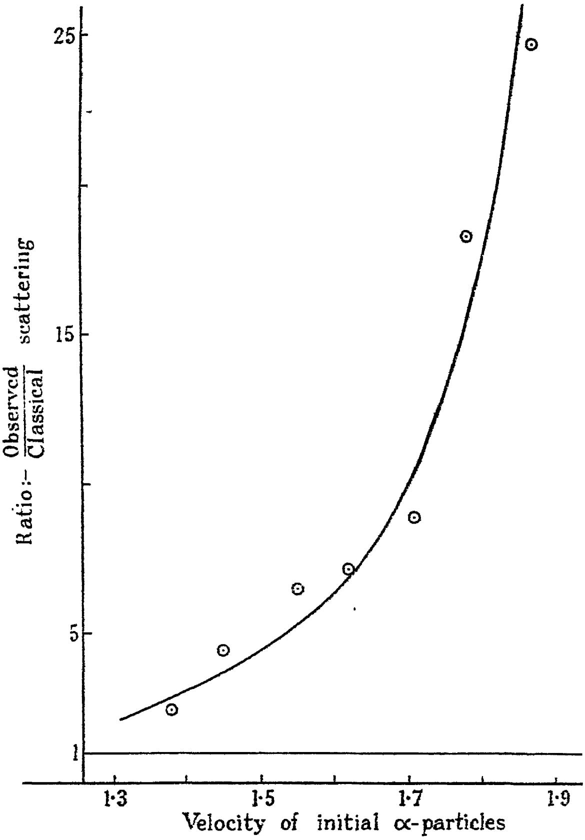

Fig. 4.

As the velocity of the α-particle is increased from $1 \cdot 4 \times 10^9$ cm./sec. the scattering increases rapidly at first, then more slowly, and for velocities greater than $1 \cdot 7 \times 10^9$ cm./sec. the increase is very rapid indeed. The slow rate of increase observed for velocities of about $1 \cdot 6 \times 10^9$ may be due to experimental error, but it seems possible, from analogy with the corresponding results from carbon shown in fig. 3, that the effect is real.

Beryllium.

The beryllium metal used in these experiments was kindly presented to me by the Siemens-Halske A.G., Berlin, to whom I wish to express my best thanks. The scattering screen was prepared in the following way. Small pieces of beryllium were broken off the specimen and these were strongly squeezed between steel plates. Small sheets of a few millimetres diameter were obtained in this way, and these were put together in the form of a mosaic on a sheet of graphite.

According to the analysis by Siemens-Halske A.G. the beryllium specimen contained about 0·5 per cent. of iron as impurity. This was confirmed by the scattering experiments, for it was observed that some α-particles were present which had ranges much greater than those of particles scattered from the beryllium itself. The maximum range of these extraneous particles was less than 5 cm. Their number was of the same order as the effect expected from the beryllium on inverse square scattering, and therefore only a small part of the total observed scattering. No particles were observed which had ranges greater than 5 cm. of air.

Only one series of experiments was carried out. Using α-particles of 6·8 cm. initial range the angular distribution of the scattered particles was determined from 127° to 160°. About 200 scintillations were counted at each angular setting. The results are given in Table VI and shown graphically in fig. 5.

Table VI.—Angular Distribution of Scattering from Beryllium for α-particles of 6·8 cm. Initial Range.

Angle.	Number of scattered particles.		
	Inverse square law.	Observed.	Ratio.
127°	0·39	3·8	9·7
133°	0·275	3·4	12·5
140°	0·18	3·3	18·5
146°	0·135	3·2	23·5
153°	0·105	4·4	43·0

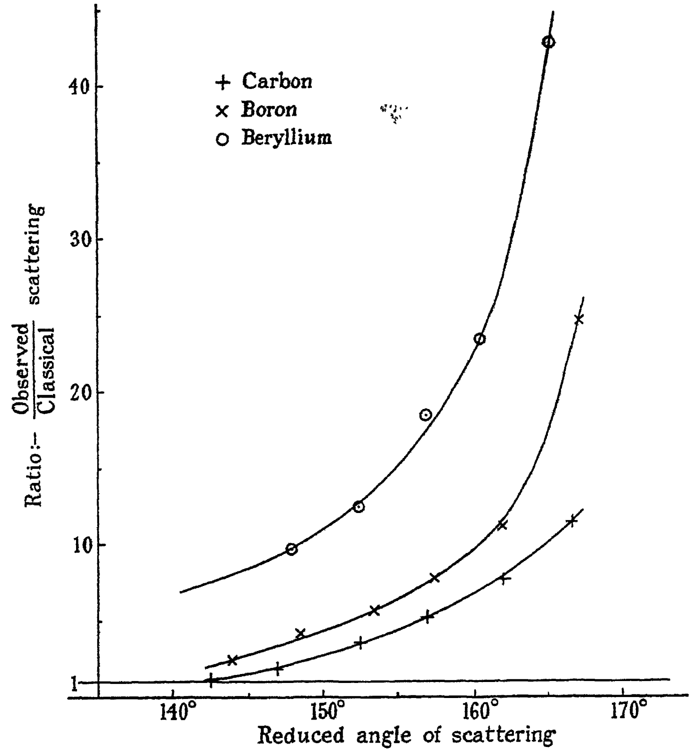

FIG. 5.

In this figure the abscissæ are not the observed angles of scattering, but the scattering angles reduced to a system of co-ordinates fixed to the centre of gravity of the colliding particles. This is more convenient for comparison with theoretical calculations. The reduced angles corresponding to those actually observed are given below for the different elements examined.

Observed angle.	127°.	133°.	140°.	146°.	153°.	160°.
Aluminium	134	139½	145½	151	157	163
Carbon	142½	147	152½	157	162	166½
Boron	144	148½	153½	157½	162	167
Beryllium	148	152½	157	160½	165	169½

They are similar to those obtained for carbon and boron, but the deviation from classical scattering is considerably greater. At the largest angle observed, the scattering is more than 40 times that expected on inverse square forces.

No observations of the variation of scattering with the velocity of the incident α-particles were made. The ranges of the particles scattered from beryllium are only about 5 per cent. of the initial range of the α-particle. The counting of the scintillations was already difficult when using α-particles of 6·8 cm. initial range, and with slower particles the experiments would have been not only more difficult but probably quite unreliable.

Discussion.

It has been shown by several authors* that the scattering of particles by a Coulomb centre of force follows exactly the same laws on the wave mechanics as on the classical theory. To explain the observed deviations from the classical theory we must therefore assume that the field between the α-particle and the nucleus deviates from a Coulomb field in the immediate neighbourhood of the nucleus. The calculation of the actual field of force from the experimental data is a very difficult problem, particularly when the wave mechanics must be used. It is possible, however, to give a general explanation of the experimental observations and to obtain a rough idea of the size of the atomic nucleus without making any special assumptions about the exact shape of the nuclear field at very close distances.

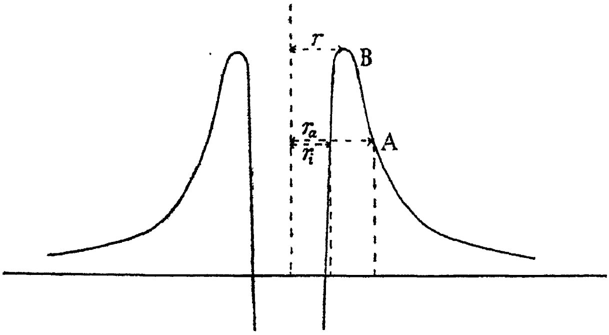

Fig. 6.

We assume that the potential of the α-particle in the field of the nucleus is of the type shown in fig. 6. We shall suppose that the field varies according to Coulomb's law, approximately at least, up to a point B not very far from the top of the potential barrier. To obtain an equation for the distribution of the scattered particles we have first to develop the plane wave, which in the wave mechanics corresponds to the beam of homogeneous incident α-particles, into spherical harmonics. The physical meaning of this operation is to separate the incident particles according to their angular momentum with regard to the scattering nucleus. To the partial wave of order l correspond the particles with the angular momentum $l \,.\, h/2\pi$, where h is Planck's constant and l is a whole number. Now consider the case in which an α-particle makes a very close collision with the nucleus and comes so high up the potential barrier that the thickness of the barrier at this point A is of the same order of magnitude as the wave-length of the α-particle. There is then a certain probability that the α-particle will penetrate the barrier. The scattered wave which represents this particle will have a certain deviation in phase (we neglect disintegration phenomena) and will so disturb the classical distribution of scattered particles, which is according to wave mechanics an interference effect of all the scattered partial waves.

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* Wentzel, 'Z. Physik.,' vol. 40, p. 590 (1927); Oppenheimer, 'Z. Physik.,' vol. 43, p. 413 (1927); Mott, 'Proc. Roy. Soc.,' A, vol. 118, p. 542 (1928); Temple, 'Proc. Roy. Soc.,' A, vol. 121, p. 673 (1928); Gordon, 'Z. Physik.,' vol. 48, p. 180 (1928).

If we now assume that in a particular case all the particles with an angular momentum less than $l \,.\, h/2\pi$ reach a distance from the centre of the nucleus so small as to allow a considerable fraction to penetrate the barrier, then all the partial waves of order l and less than l will be affected. Beck* has carried out the calculations for the two cases in which the partial waves $l = 0$ and $l = 1$ are affected.† We can see from his results that the deviations from classical scattering in general increase with increasing angle of scattering. In the case of scattering by a light nucleus the ratio of wave mechanical to classical scattering cannot be greater than about 2, even at the largest angles, if the partial wave of zero order only is disturbed. If the partial wave of first

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* Beck, 'Z. Physik,' vol. 62, p. 331 (1930).

† In the paper mentioned, Beck considers only the case when the order $l = 0$ is disturbed. He has kindly calculated for me the corresponding formula when the orders $l = 0$ and $l = 1$ are affected. The result is

$$\begin{aligned}\Sigma = 1 &+ \frac{\sin^4 \vartheta/2}{\alpha^2}\,[4q_0{}^2 \sin^2 \sigma\,(0,\alpha) + 36q_1{}^2 \cos^2 \vartheta \sin^2 \sigma\,(1,\alpha)] \\ &- 4\,\frac{\sin^2 \vartheta/2}{\alpha}\,.\,q_0 \sin \sigma\,(0,\alpha) \cos\,[\sigma\,(0,\alpha) - \alpha \log \sin^2 \vartheta/2 - \delta_0] \\ &- 12\,\frac{\cos \vartheta \sin^2 \vartheta/2}{\alpha}\,.\,q_1 \sin \sigma\,(1,\alpha) \cos\,[\sigma\,(1,\alpha) - 2\sigma\,(0,\alpha) + \alpha \log \sin^2 \vartheta/2 + \delta_1] \\ &+ 24\,\frac{\cos \vartheta \sin^4 \vartheta/2}{\alpha^2}\,q_0 q_1 \cos\,[\sigma\,(0,\alpha) - \sigma\,(1,\alpha)] \sin\left[\sigma\,(0,\alpha) + \frac{\delta_0 - \delta_1}{2}\right] \\ &\qquad\qquad\qquad\qquad \times \sin\left[\sigma\,(1,\alpha) - \frac{\delta_0 - \delta_1}{2}\right]\end{aligned}$$

where $\alpha = 4\pi Ze^2/hv$; $\sigma\,(0,\alpha) = \arg\,|\,\Gamma\,(1 + i\alpha)\,|$; $\sigma\,(1,\alpha) = \sigma\,(0,\alpha) + \operatorname{arc} tg\,\alpha$; q_0 and q_1 are constants of the order unity, δ_0 and δ_1 are phase constants. The latter four quantities cannot be calculated at present, for they depend on the shape assumed for the nuclear field.

order is also affected the ratio may at large angles be as high as 7, and, generally, the ratio will increase rapidly as further partial waves are disturbed.

In general, the ratio will increase with increasing velocity of the incident α-particle, but the variation with velocity of the particle is not necessarily a monotonic function, for it depends to a large extent on the exact shape of the internal potential field of the nucleus, about which we have as yet no sufficient information to permit even rough calculations.

Beck's calculated curve for the scattering by aluminium, when only the partial wave of zero order is affected, is very similar to the experimental curve given in fig. 2. We may therefore assume that α-particles of 6·5 cm. range which make central collisions with an aluminium nucleus have an appreciable chance of penetrating the nuclear barrier. The closest distance of approach for these particles in a Coulomb field round a nuclear charge $13e$ is $5 \cdot 6 \times 10^{-13}$ cm. The experiments show that the partial wave of first order, *i.e.*, particles with angular momentum $h/2\pi$, can at most only be slightly affected. Particles of angular momentum $h/2\pi$ and an initial range of 6·5 cm. would approach to a distance of $6 \cdot 0 \times 10^{-13}$ cm. from the aluminium nucleus. It appears, therefore, that α-particles have to reach a minimum distance (r_e in fig. 6) of about 6×10^{-13} cm. from the aluminium nucleus to be able to penetrate the nuclear barrier with an appreciable probability. We can now obtain an idea of the internal radius of the nuclear field at this level if we suppose that the scattering becomes markedly anomalous for a certain order when about half the incident α-particles of the corresponding angular momentum penetrate into the nucleus. Then, using a formula given by Gamow and Houtermans,* we find that the internal radius r_i is about half the external radius, that is, r_i is about 3×10^{-13} cm. The radius r of the top of the potential barrier must therefore lie between 3 and 6×10^{-13} cm.

Consider now the case of boron. From the experimental scattering curve of fig. 4 we should deduce that for incident α-particles of velocity $1 \cdot 4 \times 10^9$ cm./sec. the zero order is affected, the first order for incident particles of velocity $1 \cdot 5 \times 10^9$ cm./sec., and the second order for particles of velocity $1 \cdot 7 \times 10^9$ cm./sec. In fig. 7 the distance of closest approach of an α-particle to the boron nucleus is plotted as a function of its initial velocity and angular momentum, assuming that the field is Coulombian. Comparing this with the data just mentioned, we see that an α-particle must reach a distance of about $4 \cdot 8 \times 10^{-13}$ cm. from the centre of the boron nucleus if the scattering is to be anomalous, that is, if it is to have an appreciable chance of penetrating the potential barrier. Using the same argument as in the case of aluminium, we find that the internal radius r_i of the boron nucleus at this level is about $2 \cdot 4 \times 10^{-13}$ cm., and the top of the potential barrier, or " size " of the nucleus will be between these two limits.

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* Gamow and Houtermans, 'Z. Physik,' vol. 52, p. 496 (1929); Gamow, *ibid.*, vol. 52, p. 510 (1929).

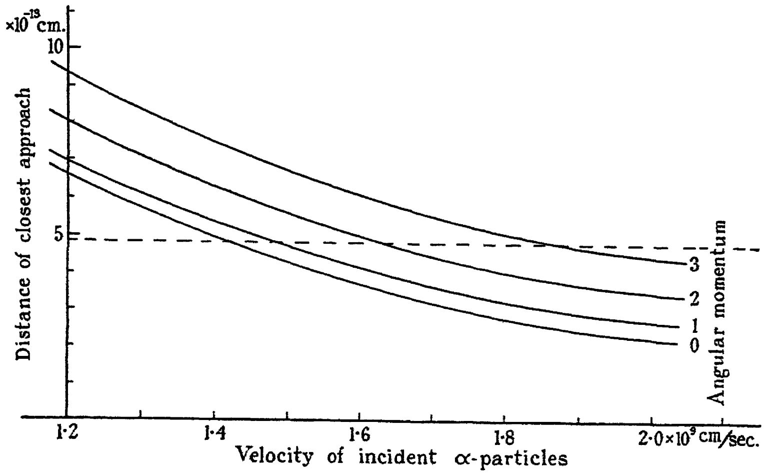

FIG. 7.

In the same way we can deduce from the experimental data on the scattering of carbon that the carbon nucleus is a few per cent. larger than the boron nucleus. As we have previously mentioned, the fact that the ratio of observed scattering to the classical scattering does not vary in a monotonic way is not in contradiction with the theory, but it is not possible to say much about the meaning of this variation without knowing more about the shape of the potential barrier.

The experimental data in beryllium are too meagre to allow any accurate deductions, but it is evident that the beryllium nucleus is, as we might expect, distinctly smaller than the boron nucleus.

Summary.

The scattering of α-particles by certain light elements, viz., beryllium, boron, carbon and aluminium, has been observed at large angles of scattering and, in some cases, for α-particles of different velocities. It was found that the scattering at the largest angles was very much greater than that calculated on the assumption of inverse square forces between the α-particle and nucleus, and that in general the deviation from classical scattering increased rapidly with the velocity of the α-particle.

A general explanation of the phenomenon has been given from the point of view of wave mechanics, and the experimental data have been used to obtain a rough idea of the size of the scattering nuclei.

I wish to express my thanks to Dr. J. Chadwick for having suggested the problem and for his continuous interest in the work, and to Dr. Guido Beck for many interesting discussions about the theoretical points of the problem.

My thanks are due to Mr. Crowe for his help in preparing the radio-active sources.

The Formation of Vortices from a Surface of Discontinuity.

By L. Rosenhead, Ph.D., St. John's College, 1851 Senior Research Student.

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1. *Introduction.*

Helmholtz* was the first to remark on the instability of those "liquid surfaces" which separate portions of fluid moving with different velocities, and Kelvin,† in investigating the influence of wind on waves in water, supposed frictionless, has discussed the conditions under which a plane surface of water becomes unstable. Adopting Kelvin's method, Rayleigh‡ investigated the instability of a surface of discontinuity. A clear and easily accessible rendering of the discussion is given by Lamb.§

The above investigations are conducted upon the well-known principle of "small oscillations"—there is a basic steady motion, upon which is superposed a flow, the squares of whose components of velocity can be neglected. This method has the advantage of making the equations of motion linear. If by this method the flow is found to be stable, the equations of motion give the subsequent history of the system, for the small oscillations about the steady state always remain "small." If, however, the method indicates that the system is unstable, that is, if the deviations from the steady state increase exponentially with the time, the assumption of small motions cannot, after an appropriate interval of time, be applied to the case under consideration, and the equations of motion, in their approximate form, no longer give a picture of the flow. For this reason, which is well known, the investigations of Rayleigh only prove the existence of instability during the initial stages of the motion. It is the object of this note to investigate the form assumed by the surface of discontinuity when the displacements and velocities are no longer small.

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* Helmholtz, 'Phil. Mag.,' vol. 36 (1868).

† Kelvin, 'Phil. Mag.,' vol. 42 (1871), or 'Collected Works,' vol. 4.

‡ Rayleigh, 'Proc. London Math. S.,' vol. 10 (1879), or 'Collected Works,' vol. 1.

§ Lamb, 'Hydrodynamics,' p. 350 (Cambridge, 1924).

In a recent paper on "The Wake in Fluid Flow Past a Solid,"* Dr. Jeffreys stated ". . . wherever the surface (of discontinuity) projects into the upper fluid the velocity of the upper fluid is increased and that of the lower diminished, by considerations of continuity; hence the changes in pressure resulting tend to push the lower fluid further into the upper. But if each wave is symmetrical about its crest, the distribution of pressure is also symmetrical. Therefore each wave must grow symmetrically, whatever its amplitude. This is not what is observed. Surfaces of discontinuity of velocity do not give symmetrical waves of large amplitude; they give series of vortices." When, however, it was pointed out to Dr. Jeffreys that a surface of discontinuity does not tend to grow symmetrically, as shown later in this paper, he detected an error in the above argument by referring to a work on "The Formation of Water Waves by Wind."† In equation (11) of his paper, with $\rho' = \rho$, $U' = -U$, $g = 0$, $T = 0$, in the general solution, we get

$$\sigma^2 + U^2 p^2 = 0.$$

If then the surface displacement ζ is given by $\zeta \propto e^{\gamma t} \cos kx$, we have

$$\gamma^2 = k^2 U^2,$$

and by inserting this in equation (8) of the same paper we see

$$\begin{aligned} \frac{P}{\rho} &= -\frac{(\sigma + Up)^2}{r}\zeta \\ &= -\frac{2\sigma U p}{r}\zeta \quad \propto \; 2\gamma U \sin kx, \end{aligned}$$

where P is the pressure, $\sigma \equiv \partial/\partial t$, $p \equiv \partial/\partial x$, and r is here some constant. We see, therefore, that the pressure is antisymmetrical instead of symmetrical with respect to the crest of a wave.

In section 3 of the present investigation a second approximation to the original Rayleigh theory is obtained. It is shown that the surface of discontinuity, instead of growing according to the formula

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* Jeffreys, 'Proc. Roy. Soc.,' A, vol. 128, p. 383 (1930).

† Jeffreys, 'Proc. Roy. Soc.,' A, vol. 107, p. 190 (1925).

$$y = a_1 e^{kUt} \cos kx,$$

obeys the law

$$y = a_1 e^{kUt} \cos kx + \tfrac{1}{2}\, Uk^2 a_1{}^2 t e^{2kUt} \sin 2kx,$$

correct to the second order of small quantities. The tendency to become unsymmetrical is shown by the second term in the equation.

The method of the Rayleigh theory, that of expressing the displacement of the surface as a Fourier series in x, whose coefficients are functions of the time, cannot show the rolling up of a surface of discontinuity, and in investigating the ultimate shape of the surface an approximate numerical method has been used. The principle of this method is that, instead of assuming a continuous distribution of vorticity over the surface, we approximate to it by assuming a distribution of finite " elemental " vortices, and we follow up the paths of these vortices by a numerical step-by-step method. The line joining these elemental vortices at any instant of time is an approximation to the actual shape of the surface at that time. A very similar idea appears to have been suggested in a letter* to 'Nature' which has recently been brought to my notice. In it A. R. Low says that in order better to understand the motion of fluids, " A mass of perfect fluid consisting of several distinct parts, each with its own velocity potential, and separated by thin sheets of transition (in the mathematical limit, vortex sheets) may be effectively redistributed . . . . . and new mean elements with an effective finite distribution of vorticity become the objects of physical observation and measurement through the whole or part of the joint mass."

In the following paper the author is greatly indebted to Professor Prandtl and to Dr. Jeffreys, whose suggestions and criticisms have greatly increased the scope of the work. Various sections of the following discussion are capable of extension and it is hoped that their results will shortly be published.

2. *Summary.*

The flow of a stream of density ρ and velocity U in the direction of the axis of x, above a stream of the same density but velocity U in the opposite direction, is investigated by the method of small oscillations and by an approximate numerical method. The motion is two-dimensional and the common surface, when undisturbed, is the axis of x. The flow on both sides of the surface of discontinuity is continuous and irrotational. Initially the disturbed surface of separation is supposed to be a sine curve of small amplitude.

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* A. R. Low, 'Nature,' vol. 121, p. 576 (1928).

The solution of the problem by the method of small oscillations is composed of two terms—a first and a second order term. The first-order term, which corresponds to the original Rayleigh solution, represents a sine curve of continuously increasing amplitude. The second-order term, which ultimately dominates, introduces a disturbance which is antisymmetrical with respect to a crest—and hence the surface of discontinuity does not grow symmetrically. The Rayleigh method can only be applied during the first stages of flow, in which the displacement can be represented by a Fourier series in x.

The motion is further investigated by means of an approximate numerical method. The surface of discontinuity, which is a vortex sheet, is replaced by a distribution of finite elemental vortices along its trace, and the paths of these vortices are determined by a numerical step-by-step method. The line joining these vortices at any instant is assumed to be an approximation to the actual shape of the surface at that time. It is shown that the effect of instability upon a surface of discontinuity of sine form is to produce concentrations of vorticity at equal intervals along the surface, and it is also shown that the surface of discontinuity tends to roll up round these points of concentration with an accompanying increase in the amplitude of the displacement. For comparison, the effect of putting 2, 4, 8, 12 elemental vortices of equal strength, initially equally spaced along the surface, is investigated, but the results are of the same nature.

The effect of diffusion, which is just mentioned qualitatively, is to retard the rolling up process. The results of the investigation are purely qualitative, but they account for the formation of vortices from a surface of discontinuity. No attempt is made to discover that value of the wave-length which ultimately becomes dominant in the disturbance, and so fixes the distance between successive vortices.

3. *The Method of Small Oscillations.*

We assume that we are dealing with the flow of a stream of density ρ and velocity U in the direction of the axis of x, above a stream of the same density but velocity U in exactly the opposite direction. The motion is two-dimensional and the common surface, when undisturbed, is the axis of x. The flow on both sides of the surface of discontinuity is continuous and irrotational. The initial form of the disturbed surface is $y = a \cos kx$, where a is of the first order of small quantities.

Following Rayleigh, we put

$$\left.\begin{aligned}\phi &= \mathrm{U}x + \phi_1 + \phi_2 \\ \phi' &= -\mathrm{U}x + \phi_1' + \phi_2'\end{aligned}\right\}, \tag{1}$$

where ϕ is the velocity potential of the upper stream and ϕ' that of the lower one. From considerations of continuity we must have that $\nabla^2\phi = 0 = \nabla^2\phi'$. We assume also that ϕ_1, ϕ_1' are of the first order, and that ϕ_2, ϕ_2' are of the second order. The form of the surface at time t is assumed to be

$$y = a\,e^{i(\sigma t - kx)} + y_2, \tag{2}$$

where σ is to be determined, and where y_2 is a function of x and t only, and is of the second order. As in other problems of a similar nature, it is appropriate to put

$$\left.\begin{aligned}\phi_1 &= \mathrm{A}e^{-ky+i(\sigma t-kx)} \\ \phi_1' &= \mathrm{A}'e^{ky+i(\sigma t-kx)}\end{aligned}\right\}, \tag{3}$$

the streams being assumed to be of infinite depth. If u, v represent the component velocities in the upper stream, u', v' those in the lower stream, the kinematical conditions to be satisfied are $\mathrm{DF}/\mathrm{D}t = 0$ at the boundary, that is

$$\left.\begin{aligned}\frac{\partial \mathrm{F}}{\partial t} + u\,\frac{\partial \mathrm{F}}{\partial x} + v\,\frac{\partial \mathrm{F}}{\partial y} &= 0 \\ \frac{\partial \mathrm{F}}{\partial t} + u'\,\frac{\partial \mathrm{F}}{\partial x} + v'\,\frac{\partial \mathrm{F}}{\partial y} &= 0\end{aligned}\right\}, \tag{4}$$

at the boundary. The expression represented by F is

$$\mathrm{F} \equiv y - a\,e^{i(\sigma t-kx)} - y_2 \equiv 0.$$

Also, the expression for the pressure in the upper stream is

$$-\frac{p}{\rho} = \frac{\partial\phi}{\partial t} + \tfrac{1}{2}(u^2+v^2) + gy,$$

and in the lower stream

$$-\frac{p'}{\rho} = \frac{\partial\phi'}{\partial t} + \tfrac{1}{2}(u'^2+v'^2) + gy,$$

so that the equation representing the continuity of pressure at the common surface is

$$\frac{\partial\phi}{\partial t}+\tfrac{1}{2}(u^2+v^2)=\frac{\partial\phi'}{\partial t}+\tfrac{1}{2}(u'^2+v'^2), \tag{5}$$

to be satisfied at the boundary.

If we only require accuracy to the first order of small quantities, equations (4) and (5) become

$$\left.\begin{aligned}\mathrm{A}k &= -\iota a(\sigma-k\mathrm{U})\\ \mathrm{A}'k &= \iota a(\sigma+k\mathrm{U})\\ \mathrm{A}(\sigma-k\mathrm{U}) &= \mathrm{A}'(\sigma+k\mathrm{U})\end{aligned}\right\}, \tag{6}$$

from which

$$(\sigma-k\mathrm{U})^2+(\sigma+k\mathrm{U})^2=0,$$

or

$$\sigma/k=\pm i\mathrm{U}. \tag{7}$$

This is the Rayleigh solution. The most general form, therefore, correct to the first order, is

$$\begin{aligned}y &= a_1e^{k\mathrm{U}t}\cos kx+a_1'e^{-k\mathrm{U}t}\cos kx,\\ \phi_1 &= a_1\mathrm{U}e^{k\mathrm{U}t-ky}(\sin kx-\cos kx)+a_1'\mathrm{U}e^{-k\mathrm{U}t-ky}(\sin kx+\cos kx),\\ \phi_1' &= a_1\mathrm{U}e^{k\mathrm{U}t+ky}(\sin kx+\cos kx)+a_1'\mathrm{U}e^{-k\mathrm{U}t+ky}(\sin kx-\cos kx),\end{aligned}$$

where a_1 and a_1' are of the first order and satisfy the relation

$$a_1+a_1'=a.$$

The above values are incorporated in the general equations, and the following eight relations give the value at the common surface, correct to the second order, of the relevant expressions. (For simplicity we here introduce the abbreviations $s\equiv\sin kx$, $c\equiv\cos kx$.)

$$\begin{aligned}\frac{\partial\phi}{\partial t} &= k\mathrm{U}^2[a_1e^{k\mathrm{U}t}(s-c)-a_1'e^{-k\mathrm{U}t}(s+c)]+\frac{\partial\phi_2}{\partial t}\\ &\qquad -k^2\mathrm{U}^2[a_1^2e^{2k\mathrm{U}t}(sc-c^2)-a_1'^2e^{-2k\mathrm{U}t}(sc+c^2)-2a_1a_1'c^2],\\ \frac{\partial\phi}{\partial x} &= \mathrm{U}+k\mathrm{U}[a_1e^{k\mathrm{U}t}(s+c)-a_1'e^{-k\mathrm{U}t}(s-c)]+\frac{\partial\phi_2}{\partial x}\\ &\qquad -k^2\mathrm{U}[a_1^2e^{2k\mathrm{U}t}(sc+c^2)-a_1'^2e^{-2k\mathrm{U}t}(sc-c^2)+2a_1a_1'c^2],\\ \frac{\partial\phi}{\partial y} &= -k\mathrm{U}[a_1e^{k\mathrm{U}t}(s-c)+a_1'e^{-k\mathrm{U}t}(s+c)]+\frac{\partial\phi_2}{\partial y}\\ &\qquad +k^2\mathrm{U}[a_1^2e^{2k\mathrm{U}t}(sc-c^2)+a_1'^2e^{-2k\mathrm{U}t}(sc+c^2)+2a_1a_1'sc],\end{aligned}$$

$$\begin{aligned}
\tfrac{1}{2}(u^2+v^2) &= \tfrac{1}{2}U^2 + kU^2[a_1e^{kUt}(s+c) - a_1'e^{-kUt}(s-c)] + U\frac{\partial\phi_2}{\partial x}\\
&\quad + k^2U^2[a_1{}^2e^{2kUt}(s^2-sc) + a_1'^2e^{-2kUt}(s^2+sc) - a_1a_1'c^2],\\
\frac{\partial\phi'}{\partial t} &= kU^2[a_1e^{kUt}(s+c) - a_1'e^{-kUt}(s-c)] + \frac{\partial\phi_2'}{\partial t}\\
&\quad + k^2U^2[a_1{}^2e^{2kUt}(sc+c^2) - a_1'^2e^{-2kUt}(sc-c^2) + 2a_1a_1'c^2],\\
\frac{\partial\phi'}{\partial x} &= -U - kU[a_1e^{kUt}(s-c) - a_1'e^{-kUt}(s+c)] + \frac{\partial\phi_2'}{\partial x}\\
&\quad - k^2U[a_1{}^2e^{2kUt}(sc-c^2) - a_1'^2e^{-2kUt}(sc+c^2) - 2a_1a_1'c^2],\\
\frac{\partial\phi'}{\partial y} &= kU[a_1e^{kUt}(s+c) + a_1'e^{-kUt}(s-c)] + \frac{\partial\phi_2'}{\partial y}\\
&\quad + k^2U[a_1{}^2e^{2kUt}(sc+c^2) + a_1'^2e^{-2kUt}(sc-c^2) + 2a_1a_1'sc],\\
\tfrac{1}{2}(u'^2+v'^2) &= \tfrac{1}{2}U^2 + kU^2[a_1e^{kUt}(s-c) - a_1'e^{-kUt}(s+c)] - U\frac{\partial\phi_2}{\partial x}\\
&\quad + k^2U^2[a_1{}^2e^{2kUt}(s^2+sc) + a_1'^2e^{-2kUt}(s^2-sc) - a_1a_1'c^2].
\end{aligned}$$

With these values the kinematical conditions become

$$\left.\begin{aligned}
\frac{\partial y_2}{\partial t} + U\frac{\partial y_2}{\partial x} - \frac{\partial\phi_2}{\partial y} &= k^2U[a_1{}^2e^{2kUt}(\sin 2kx - \cos 2kx)\\
&\quad + a_1'^2e^{-2kUt}(\sin 2kx + \cos 2kx) + 2a_1a_1'\sin 2kx]\\
\frac{\partial y_2}{\partial t} - U\frac{\partial y_2}{\partial x} - \frac{\partial\phi_2'}{\partial y} &= k^2U[a_1{}^2e^{2kUt}(\sin 2kx + \cos 2kx)\\
&\quad + a_1'^2e^{-2kUt}(\sin 2kx - \cos 2kx) + 2a_1a_1'\sin 2kx]
\end{aligned}\right\}, \tag{8}$$

and the equation for the continuity of pressure is

$$\begin{aligned}
&\frac{\partial\phi_2}{\partial t} + U\frac{\partial\phi_2}{\partial x} - k^2U^2[a_1{}^2e^{2kUt} - a_1'^2e^{-2kUt}]\sin 2kx\\
&\qquad = \frac{\partial\phi_2'}{\partial t} - U\frac{\partial\phi_2'}{\partial x} + k^2U^2[a_1{}^2e^{2kUt} - a_1'^2e^{-2kUt}]\sin 2kx,
\end{aligned} \tag{9}$$

to be satisfied at $y = 0$. Equations (8) and (9) can be re-arranged as follows :

$$\left.\begin{aligned}
\frac{\partial\phi_2}{\partial y} &= \frac{\partial y_2}{\partial t} + U\frac{\partial y_2}{\partial x} - k^2U[\sin 2kx\,(a_1e^{kUt} + a_1'e^{-kUt})^2\\
&\quad - \cos 2kx\,(a_1{}^2e^{2kUt} - a_1'^2e^{-2kUt})]\\
\frac{\partial\phi_2'}{\partial y} &= \frac{\partial y_2}{\partial t} - U\frac{\partial y_2}{\partial x} - k^2U[\sin 2kx\,(a_1e^{kUt} + a_1'e^{-kUt})^2\\
&\quad + \cos 2kx\,(a_1{}^2e^{2kUt} - a_1'^2e^{-2kUt})]
\end{aligned}\right\}, \tag{10}$$

$$\frac{\partial}{\partial t}(\phi_2 - \phi_2') + U\frac{\partial}{\partial x}(\phi_2 + \phi_2') = 2k^2U^2\sin 2kx\,[a_1{}^2e^{2kUt} - a_1'^2e^{-2kUt}]. \tag{11}$$

From these equations it is evident that y_2 can be expressed in the form $P\cos 2kx + \phi\sin 2kx$. (A rigorous proof of this can easily be obtained by a simple refinement of the following argument.) It follows therefore that the values of ϕ_2 and ϕ_2' when y is not zero, are

$$\left.\begin{aligned}\phi_2 &= -\frac{e^{-2ky}}{2k}\left\{\frac{\partial y_2}{\partial t} + U\frac{\partial y_2}{\partial x} - k^2U\left[\sin 2kx\,(a_1e^{kUt} + a_1'e^{-kUt})^2\right.\right.\\ &\qquad\qquad\left.\left. - \cos 2kx\,(a_1^2e^{2kUt} - a_1'^2e^{-2kUt})\right]\right\}\\ \phi_2' &= \frac{e^{2ky}}{2k}\left\{\frac{\partial y_2}{\partial t} - U\frac{\partial y_2}{\partial x} - k^2U\left[\sin 2kx\,(a_1e^{kUt} + a_1'e^{-kUt})^2\right.\right.\\ &\qquad\qquad\left.\left. + \cos 2kx\,(a_1^2e^{2kUt} - a_1'^2e^{-2kUt})\right]\right\}\end{aligned}\right\}. \tag{12}$$

and hence

$$\frac{\partial}{\partial t}(\phi_2 - \phi_2') = -\frac{1}{k}\frac{\partial^2 y_2}{\partial t^2} + 2k^2U^2(a_1^2e^{2kUt} - a_1'^2e^{-2kUt}),$$

$$U\frac{\partial}{\partial x}(\phi_2 + \phi_2') = -\frac{U^2}{k}\frac{\partial^2 y}{\partial x^2} + 2k^2U^2(a_1^2e^{2kUt} - a_1'^2e^{-2kUt}),$$

so that on substituting in (11) we get

$$\frac{\partial^2 y_2}{\partial t^2} + U^2\frac{\partial^2 y_2}{\partial x^2} = 2k^3U^2(a_1^2e^{2kUt} - a_1'^2e^{-2kUt})\sin 2kx. \tag{13}$$

We require only the "particular" solution of this equation, whence it follows that

$$y_2 = \tfrac{1}{2}Uk^2t\,(a_1^2e^{2kUt} + a_1'^2e^{-2kUt})\sin 2kx. \tag{14}$$

The amplitude of the disturbance represented by y_2 grows much more rapidly than that of $(a_1e^{kUt} + a_1'e^{-kUt})\cos kx$, and ultimately dominates it. The expression represented by y_2 is also antisymmetrical with respect to $x = 0$, that is with respect to a crest of the original wave, and its effect, as t increases, is to give the original cosine curve a shape somewhat like that of a breaker in the first stages of its growth, instead of the symmetrical shape suggested by the Rayleigh solution. Ultimately, of course, when t is very big, the surface, according to this theory, is virtually a sine curve of period π/k instead of a cosine curve of period $2\pi/k$. The theory, however, is not applicable when t is large, for by that time the third and higher order terms can no longer be neglected. In addition, a picture of the actual ultimate state of affairs cannot be obtained without introducing diffusion and viscosity. It is evident, too, that the method of representing the displacement y by a Fourier series in x cannot show the rolling up of the surface, and is, as a matter of fact, only valid during the first stages of the motion. The following sections describe a method which gives the form of the surface without being subject to this restriction.

4. *An Approximate Solution.*

An approximation to the surface of discontinuity, which is a vortex sheet, can be obtained by replacing the continuous distribution of vorticity by isolated vortices of appropriate strength along its trace. We shall not investigate the effect of a general disturbance involving all wave-lengths, but shall restrict ourselves to one particular wave-length. The final result cannot be obtained by superposing the effects of the separate wave-lengths, but the general nature of the flow is the same for each component wave. We can imagine that the wave-length considered is the one that ultimately dominates as a result of instability, and so fixes the distance between successive vortices of the resulting system. The actual determination of this wave-length is not here attempted, and it seems probable that this can only be done by taking diffusion and viscosity into account.

4.1. *Two Vortices to a Wave-length.*—As a preliminary step we investigate the case of two vortices to a wave-length, and the system reduces to a single row of vortices of strength $-\kappa$ equally spaced along the x axis. This system is in a steady state, but, as is well known,* it is unstable. If we assume, following Lamb, that the distance between consecutive vortices is $\lambda/2$, and that the mth vortex, initially at $(m\lambda/2, 0)$, suffers a displacement

$$x_m = \alpha e^{\iota m\phi}, \qquad y_m = \beta e^{\iota m\phi},$$

where ϕ lies between 0 and 2π, then we get

$$\frac{d\alpha}{dt} = \mu\beta, \qquad \frac{d\beta}{dt} = \mu\alpha,$$

where

$$\mu = \frac{4\kappa}{\pi\lambda^2}\left(\frac{1-\cos\phi}{1^2} + \frac{1-\cos 2\phi}{2^2} + \frac{1-\cos 3\phi}{3^2}\dots\right) = \frac{\kappa}{\pi\lambda^2}\,\phi\,(2\pi - \phi). \qquad (1)$$

Since the velocity of the stream above the vortices is U and that below is $-$U, then $\kappa = \lambda$U, and

$$\mu = \frac{\text{U}}{\pi\lambda}\,\phi\,(2\pi - \phi).$$

We see that the component of the disturbance that grows most quickly is that for which $\phi = \pi$, and if we replace the whole disturbance by the most rapidly growing component, we have

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* Lamb, 'Hydrodynamics,' p. 208 (Cambridge, 1924).

$$x_m = (\mathrm{A}e^{\mu_1 t} + \mathrm{B}e^{-\mu_1 t})\,(-)^m, \qquad y_m = (-\mathrm{A}e^{\mu_1 t} + \mathrm{B}e^{-\mu_1 t})\,(-)^m,$$

where

$$\mu_1 = \pi\mathrm{U}/\lambda.$$

In this type of disturbance consecutive vortices are displaced to the same extent but in opposite directions. In this case the vortices depart from their initial position along arms of rectangular hyperbolæ given by the formula

$$x_m^{\,2} - y_m^{\,2} = 4\mathrm{AB}. \tag{2}$$

These paths are shown by the broken curves in fig. 1A.

The preceding theory is, however, only a first approximation, and if we can assume that the whole disturbance can be represented effectively by the component that ultimately becomes dominant, an exact theory can be applied as follows. The vortices are in the positions $\left(m\frac{\lambda}{2} + x_m, y_m\right)$ where $x_m = (-)^m x_0$, $y_m = (-)^m y_0$, and can therefore be separated into two rows

$$\left(2m\frac{\lambda}{2} + x_0, y_0\right) \quad \text{and} \quad \left((2m+1)\frac{\lambda}{2} - x_0, -y_0\right).$$

In the subsequent motion, by symmetry, the vortices will be at

$$(m\lambda + x, y), \qquad \left((2m+1)\frac{\lambda}{2} - x, -y\right)$$

where x and y vary. The exact velocity components of the vortex at (x, y) are

$$u = \frac{\kappa}{2\lambda}\,\frac{\sinh\frac{4\pi y}{\lambda}}{\cosh\frac{4\pi y}{\lambda} + \cos\frac{4\pi x}{\lambda}},$$

$$v = \frac{\kappa}{2\lambda}\,\frac{\sin\frac{4\pi x}{\lambda}}{\cosh\frac{4\pi y}{\lambda} + \cos\frac{4\pi x}{\lambda}},$$

and the paths of the vortices are

$$\frac{u}{v} = \frac{dx}{dy} = \frac{\sinh\frac{4\pi}{\lambda}y}{\sin\frac{4\pi}{\lambda}x},$$

or

$$\cosh\frac{4\pi}{\lambda}y + \cos\frac{4\pi}{\lambda}x = \cosh\frac{4\pi}{\lambda}y_0 + \cos\frac{4\pi}{\lambda}x_0. \tag{3}$$

This curve is an undulating one repeating itself at intervals of $\lambda/2$, as shown by the unbroken lines in fig. 1A, and to a first approximation is identical with that of equation (2).

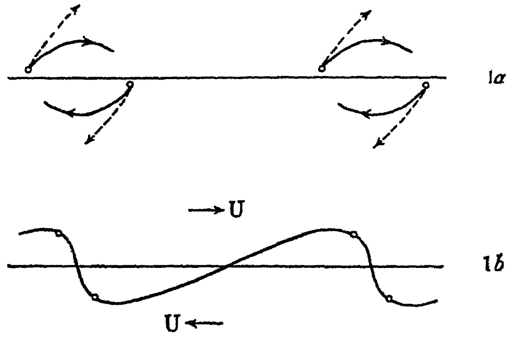

FIG. 1.

This method suggests then that, owing to instability, a single row of vortices splits itself into two rows travelling in opposite directions, the vortices themselves moving in an undulatory path. Further, the paths of the vortices suggest to some extent the turbulent nature of the flow in the wake behind a solid. The distribution of vortices according to this method is a good approximation to the surface of discontinuity only in the first stages of the flow, but even here the rolling up of the surface is suggested, as in fig. 1B. A more accurate approximation is obtained, as in the later sections, by putting more vortices into each wave-length.

It was suggested to me, however, by Dr. Jeffreys that it would be interesting to see what happens to a single undulation on a surface of discontinuity as the elemental vortices might immediately roll up into a vortex somewhere near the undulation. Section 4.2 discusses this case.

4.2. *A Single Undulation on a Surface of Discontinuity.*—As an approximation the system is replaced by a row of vortices of equal strength $-\kappa$, the distance between consecutive vortices being a. The undulation is represented by a displacement of one of the vortices through a distance h perpendicular to the row, as in fig. 2. The system is not a steady one, and if u_r, v_n are the velocity components of the nth vortex, the one initially at the origin having the number 0 attached to it, we have that the initial velocities of the vortices are

$$\left.\begin{aligned} u_0 &= \frac{\kappa}{2a}\,\frac{\sinh 2\pi\dfrac{h}{a}}{\cosh\dfrac{2\pi h}{a}-1} - \frac{\kappa}{2\pi h} = \frac{\kappa}{2a}\left[\coth\pi\frac{h}{a} - \frac{1}{\pi h/a}\right] > 0, \\ v_0 &= 0, \end{aligned}\right\} \qquad (4)$$

$$\left.\begin{aligned} u_n &= -\frac{\kappa}{2\pi}\frac{h}{h^2+n^2a^2} \\ v_n &= -\frac{\kappa}{2\pi}\frac{na}{h^2+n^2a^2}+\frac{\kappa}{2\pi}\frac{1}{na} = \frac{\kappa}{2\pi}\frac{h^2}{na\,(h^2+n^2a^2)} \end{aligned}\right\}, \tag{5}$$

and so $v_n/u_n = -h/na$.

Vortex 0 therefore moves downstream. Vortices 1 to ∞ move towards vortex 0, and numbers -1 to $-\infty$ move away from it, as shown by the arrows in fig. 2.

Without going more deeply into the matter it seems plausible to suggest that vortices $0, 1, 2, \ldots, \infty$, are going to combine to form one vortex that will travel in the direction of the positive x-axis, while vortices $-1, -2, \ldots, -\infty$, will unite to form a vortex more slowly in the direction of the negative x axis, and that there will be a rupture of the surface of discontinuity between vortices 0 and -1.

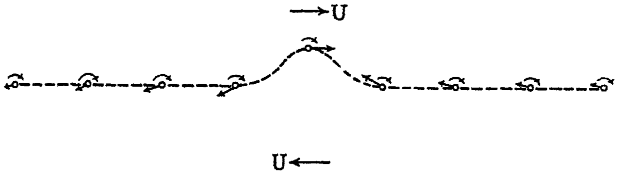

FIG. 2.

4.3. *Four Vortices to a Wave-length.*—Initially the vortices are at $\left(m\frac{\lambda}{2}, 0\right)$; $((m+\frac{1}{4})\lambda, h)$; $((m+\frac{3}{4})\lambda, -h)$, as an approximation to a sine curve of amplitude h. By symmetry, the vortices at $\left(m\frac{\lambda}{2}, 0\right)$ will always be at rest, and the other vortices will form two rows, representative members of which will be the points $((m+\frac{1}{4})\lambda+x_1, y_1)$; $((m+\frac{3}{4})\lambda-x_1, -y_1)$. The velocity components of the vortex at (x_1, y_1) is

$$u = \frac{3\kappa}{2\lambda}\frac{\sinh 4\pi\frac{y_1}{\lambda}}{\cosh 4\pi\frac{y_1}{\lambda}+\cos 4\pi\frac{x_1}{\lambda}}, \quad v = \frac{3\kappa}{2\lambda}\frac{\sin 4\pi\frac{x_1}{\lambda}}{\cosh 4\pi\frac{y_1}{\lambda}+\cos 4\pi\frac{x_1}{\lambda}},$$

and as in 4.1, the path of the vortex is

$$\cosh 4\pi\frac{y_1}{\lambda}+\cos 4\pi\frac{x_1}{\lambda} = \cosh 4\pi\frac{h}{\lambda}+1. \tag{6}$$

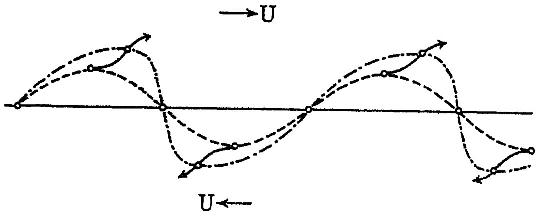

FIG. 3.

NOTE.—The — — — — line is the original form of the surface. The — . — . — . line is the form at some subsequent time. The ———— lines are the paths of the vortices.

Here again the vortices split themselves into two sections which move in opposite directions along sinuous curves.

4.4. *Eight and Twelve Vortices to a Wave-length.*—The cases of eight and twelve vortices to a wave-length will now be discussed in some detail, as they are better approximations than those considered above, to the continuous distribution of vorticity. A comparison of the various cases considered is of importance because the solution here given is a numerical one, and at first glance it is not evident whether an increase in the number of vortices to a wave-length slows down, or accelerates, the characteristic motion of the surface of discontinuity. We have seen, however, that the cases corresponding to $n = 2$ or 4 show, during the first stages of the motion, a tendency to roll up like a succession of breakers, but these cases cannot be accepted as showing the formation of vortices, for the elemental vortices show no tendency to concentrate themselves at intervals along the surface. In view of the drastic nature of the approximation it is not surprising that this is so, but it is rather remarkable that with $n = 8$ the phenomenon of the rolling up is quite evident, and certain of the vortices rotate, and continue to rotate, round the points of concentration and show no tendency to move away. This is much more evident with $n = 12$, and so we are led to believe that an increase in the number of elemental vortices to the wave-length accelerates the rolling up process. This can be seen more explicitly by a comparison of Tables I and II, which correspond to $n = 8$ and $n = 12$ respectively. The " concentration " process is much more in evidence in the latter of these cases. The numerical solution has not been continued far enough to show whether all the vortices maintain their connection with the surface or whether some of them travel away. It is very likely that those furthest away (in each wave-length) from the points of concentration move away from the system.

For the sake of simplicity therefore we shall assume that the surface of separation is a sine curve of wave-length λ whose amplitude increases according to the Rayleigh theory until it is equal to $\alpha\lambda$ (say). The curve $y = a e^{k\mathrm{U}t} \cos kx$ gives a picture of the motion, until $\left(\frac{a}{\lambda} e^{k\mathrm{U}t}\right)^2$ can no longer be neglected, and if we are working to an accuracy of 1 per cent. the Rayleigh theory can be applied until

$$t = \frac{\lambda}{2\pi\mathrm{U}} \log (\lambda/10a).$$

If a/λ should be equal to 1/100 (say) at $t = 0$, then the form given above is valid during the interval $t = 0$ to $t = 0\cdot35\ \lambda/\mathrm{U}$ second. In other words the ratio $ae^{k\mathrm{U}t}/\lambda$ increases from 1/100 to 1/10 in the time $0\cdot35\ \lambda/\mathrm{U}$ second. For the purposes of the following work the origin of time is taken at the instant where $\alpha = 1/10$. The equation of the surface of separation is then

$$y = \alpha\lambda \sin 2\pi x/\lambda,$$

or putting $y/\lambda = \eta, \quad x/\lambda = \xi,$

$$\eta = \alpha \sin 2\pi\xi. \tag{7}$$

The normal velocity on both sides of the surface of separation is continuous, but the tangential component has an abrupt discontinuity at the surface. In other words, we are dealing with a vortex sheet. If ds_0 be an element of length of the sheet in the x, y plane, dx_0 its projection on the x-axis, then the strength of vorticity at a point x on the sheet is given by the relation*

$$\kappa ds_0 + \mathrm{U}dx_0 - (-\mathrm{U})\, dx_0 = 0,$$

or

$$\kappa = -2\mathrm{U}\, dx/ds. \tag{8}$$

Since the surface of separation repeats itself at intervals of λ we may consider our system as being formed by the juxtaposition of rows of vortices of strength κds $(= -2\mathrm{U}\, dx)$, the interval between members of the row being λ, as in fig. 4, *a*, if we imagine the whole of the surface of discontinuity filled with elemental vortices. The complex potential, however, for a row of vortices of strength κ and interval λ is known, and from it, by integration, we can build up the stream function for a surface of separation of any form. The complex potential for a row of vortices of strength κ_0 and interval λ is

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* This relation is obtained by taking the circulation round the contour bounded by the lines $x = x_0$, $x = x_0 + \delta x_0$, $y = \mathrm{R}$, $y = -\mathrm{R}$, with R tending to infinity. Equation (8) is obtained on the assumption that the contributions to the circulation from the lines $x = x_0$, $x = x_0 + \delta x_0$ cancel, but Professor Prandtl pointed out that these lines may yield a small first-order term. The value of κ given by (8) can, however, be accepted as a very good approximation.

$$w = -\frac{\iota\kappa_0}{2\pi}\log\sin\pi(z-z_0)/\lambda,$$

where one of the vortices is at z_0. The components of velocity at a point (x_1, y_1) are

$$u = -\frac{\kappa_0}{2\lambda}\frac{\sinh k(y_1-y_0)}{\cosh k(y_1-y_0)-\cos k(x_1-x_0)},$$

$$v = \frac{\kappa_0}{2\lambda}\frac{\sin k(x_1-x_0)}{\cosh k(y_1-y_0)-\cos k(x_1-x_0)}.$$

The components of velocity at a point (x_1, y_1) due to the vorticity of the surface of separation are therefore

$$\left.\begin{aligned} u &= -\oint_x^{x+\lambda}\frac{\kappa ds}{2\lambda}\frac{\sinh k(y_1-y)}{\cosh k(y_1-y)-\cos k(x_1-x)} \\ v &= \oint_x^{x+\lambda}\frac{\kappa ds}{2\lambda}\frac{\sin k(x_1-x)}{\cosh k(y_1-y)-\cos k(x_1-x)} \end{aligned}\right\}, \tag{9}$$

where the integrals are line integrals taken over the surface of separation between any two limits of x differing by a wave-length. We may therefore put

$$\left.\begin{aligned} u &= \frac{U}{\lambda}\oint_0^{\lambda}\frac{\sinh k(y_1-y)}{\cosh k(y_1-y)-\cos k(x_1-x)}\,dx, \\ v &= -\frac{U}{\lambda}\oint_0^{\lambda}\frac{\sin k(x_1-x)}{\cosh k(y_1-y)-\cos k(x_1-x)}\,dx \end{aligned}\right\}. \tag{10}$$

If the point (x_1, y_1) lies above or below the surface of separation, the integrals (10) are line integrals with no singularities on the contour of integration. If, however, we wish to find the velocity of a point on the surface of separation, the integrals have a simple infinity at the point whose velocity we desire to find, and in the usual way the " principal values " of the integrals give the velocity components. We are not dealing with a problem in steady motion for the form of the surface of separation alters with time; y is a function of x and t. If the equation of the surface of separation is given by $F(x, y, t) = 0$, then the equation must satisfy the condition

$$\frac{DF}{Dt} = \frac{\partial F}{\partial t} + u\frac{\partial F}{\partial x} + v\frac{\partial F}{\partial y} = 0, \tag{11}$$

where u and v are given by (6). This is the condition that a point on the surface of separation at time t is on the new position of the surface at time $t + \delta t$.

The exact solution of (10) and (11) is a matter of some difficulty, and in attempting to obtain an approximate solution we introduce the following simplification. Instead of having a continuous distribution of vorticity over the surface of separation, we assume that the surface is broken up into many parts by lines at equal intervals of x, and the vorticity in each of these sections is imagined concentrated into an elemental vortex at its "centre of gravity"—so that our approximate picture is exactly as shown in fig. 4, *a*. We now investigate the motion of these vortices, and at any time the line joining them gives an approximation to the form of the surface of discontinuity. If we insert n vortices at equal intervals between $x = 0$ and $x = \lambda$, we put, as an approximation

$$n\kappa = -2U\lambda, \tag{12}$$

where κ is the strength of each of these elemental vortices.

The velocity of a vortex at a point (x_1, y_1) is thus given by

$$\left.\begin{aligned} u &= \frac{U}{n}\Sigma\frac{\sinh k(y_1-y)}{\cosh k(y_1-y)-\cos k(x_1-x)} \\ v &= -\frac{U}{n}\Sigma\frac{\sin k(x_1-x)}{\cosh k(y_1-y)-\cos k(x_1-x)} \end{aligned}\right\}, \tag{13}$$

or

$$\left.\begin{aligned} \frac{u}{U} &= \frac{1}{n}\Sigma\frac{\sinh 2\pi(\eta_1-\eta)}{\cosh 2\pi(\eta_1-\eta)-\cos 2\pi(\xi_1-\xi)} \\ \frac{v}{U} &= -\frac{1}{n}\Sigma\frac{\sin 2\pi(\xi_1-\xi)}{\cosh 2\pi(\eta_1-\eta)-\cos 2\pi(\xi_1-\xi)} \end{aligned}\right\}, \tag{13A}$$

the summation being over all values of (x, y) which are the co-ordinates of the other vortices. The exact solution of this problem is also difficult, for if we assume that the vortices lie on the curve $F_1(x, y, t) = 0$, then the differential equation to be satisfied by F_1 is

$$\frac{\partial F_1}{\partial t} + u\frac{\partial F_1}{\partial x} + v\frac{\partial F_1}{\partial y} = 0,$$

where u and v are given by (13). The exact solution of this problem is probably more complicated than that of the previous one, for here we have summations over a finite number of points instead of integrals over a range.

We can, however, adopt a method which is virtually a numerical solution of the differential equation. We assume that the surface of separation increases in amplitude uniformly until it is given by the equation $\eta = \alpha \sin 2\pi\xi$. We approximate to the subsequent shape of this surface by assuming in every wave-length, instead of a continuous distribution of vorticity, n elemental vortices each of strength $-2U\lambda/n$ initially uniformly spaced along the curve at intervals whose projections on the x-axis are λ/n. We now investigate the motion of the vortices numerically. The instantaneous velocities of the vortices in their initial positions, (u_1, v_1) are calculated by (13), and as an approximation the position of a vortex, initially at (x_1, y_1), at time δt_1 is $(x_1 + u_1 \delta t_1, y_1 + v_1 \delta t_1) = (x_2, y_2)$. The instantaneous velocities at (x_2, y_2) are calculated from (13), and the positions after another interval of time δt_2 are $(x_2 + u_2 \delta t_2, y_2 + v_2 \delta t_2) = (x_3, y_3)$, and so on for any number of times. The line joining all the positions (x_1, y_1) gives the form of the surface from which we commence our approximation. The line joining the points (x_2, y_2) gives the form at time δt_1 later, and the points (x_3, y_3) give the curve after a further interval δt_2, and so on. The errors introduced at each step are of the order

$$\left|\frac{u}{\lambda}\,\delta t\right|^2.$$

The order of the error can be reduced by increasing the amount of calculation and using the Kutta-Runge method, or some such process of numerical solution, but after the rather drastic approximation of imagining the surface split into elemental vortices, there is very little point in introducing a higher order of accuracy into the numerical calculations at the cost of much labour. Care, however, is taken in choosing the intervals δt in such a way that the directions of the motion of a vortex before and after any interval of time do not differ greatly.

The above method of approximation is useful only if the curvature of the paths travelled by the vortices is small, but it is useless when the curvature is large as in the case of vortices 4, 5, 7, 8 of fig. 4, *d*. In these cases the angular velocity round vortex 6, and not the linear velocity, remains approximately constant during the interval of time from $0{\cdot}35\lambda/U$ second to $0{\cdot}40\lambda/U$ second. Also this method cannot be used for a large number of steps, for the accumulation of the errors introduced at each step may become large enough to destroy the value of the approximation.

In actual practice, however, diffusion of vorticity plays an important rôle, so that if U is small the surface of separation may " disappear " before the rolling-up becomes evident. It should also be remembered that we are only considering the motion of one of the components of the general disturbance, and that all these components tend to act in the same way.

4.5. *Numerical Evaluation.*—The equations of motion of the surface have been put into a non-dimensional form and the only quantities to which numerical values have to be given are n, the number of elemental vortices per wave-length, and α, the ratio of the initial amplitude of the surface to its wave-length.

Let us compare the initial distributions of velocity along surfaces of sine form but of different amplitudes. When the amplitude is small we see that

$$u/U = (\text{amplitude}) \times g\,(x),$$
$$v/U = (\text{amplitude})^2 \times h\,(x),$$

where $g\,(x)$ and $h\,(x)$ are functions that vary along the surface. Hence a change in the amplitude, when it is small, will produce a proportionately larger change in the x-velocity than in the y-velocity. Further, if one considers the surface made up of rectilinear vortices, it can easily be seen that the crests of the wave move along the positive x-axis, and the troughs along the negative x-axis, corresponding to the directions of the upper and lower streams. At the first instant of motion also, vortices at equal distances on either side of a crest (or trough) have their x-velocities equal, but their y-velocities equal and opposite. Hence at first the surface tends to roll over itself like a breaker, and the bigger the initial amplitude the more marked is this tendency, but the general nature

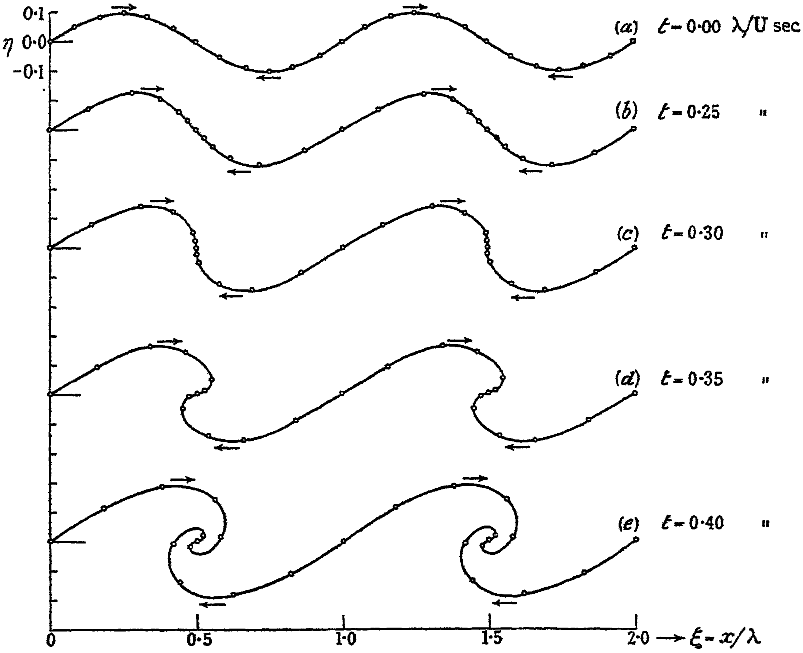

FIG. 4.

of the flow is the same in all cases. In order to avoid undue calculation we therefore take α to be rather large, say 1/10, as this should show the change in the form of the surface sooner than surfaces of smaller amplitude (see fig. 4). A more exact picture of the flow would be obtained if the initial amplitude were taken much smaller, say 1/100, but with such small values the Rayleigh theory can be applied to the system, with the modification that the surface does not maintain its sine-form as its amplitude grows, but it becomes distorted to a shape very similar to that of fig. 4, *b*. After this the small oscillations method cannot be applied and the subsequent forms are given by the approximate theory sketched above.

We therefore take the surface of discontinuity to be

$$y = 0 \cdot 1 \ \lambda \sin 2\pi x/\lambda,$$

or

$$\eta = 0 \cdot 1 \sin 2\pi\xi,$$

at time $t = 0$, and investigate the motion. We put $n = 8$, and divide the surface in such a way that there are elemental vortices at the points $r\lambda/2$, where r assumes all integral values from $-\infty$ to $+\infty$. The remaining ones are uniformly spaced between these points. Owing to the symmetry that is bound to exist during the subsequent motion, the vortices at $x = r\lambda/2$ have zero velocity for all time for they are points of antisymmetry with respect to the system. The shapes are calculated from Table I, which is self-explanatory. An increased accuracy in determining the shape of the surface would be obtained by taking n larger than 8, and such a case is given by Table II which corresponds to $n = 12$.

The general features of the flow are well marked. The various quantities in Tables I and II are given in non-dimensional form and can be applied to any other case in which α is equal to 1/10 at $t = 0$ second.

The diagrams, which are only shown for the more accurate case $n = 12$, show several well-known features. The elemental vortices appear to concentrate at intervals along the surface equal to the wave-length of the disturbance—which may be interpreted as demonstrating a periodic concentration of vorticity when a surface of discontinuity breaks up. The process of the concentration of vorticity is accompanied by a rolling up of the surface of discontinuity, which is a characteristic that has been noted by many investigators. The numerical calculation is ended at time $t = 0 \cdot 40 \ \lambda/\mathrm{U}$ second for the case $n = 12$, but the rolling up process proceeds with increased rapidity for the elemental vortices in the neighbourhood of vortex No. 6 have a large

Table I.—$n = 8$.

Vortex No.	Co-ordinates at $t = 0·00$ sec.		Velocity components at $t = 0·00$ sec.		Co-ordinates at $t = 0·10$ λ/U sec.		Velocity components at $t = 0·10$ λ/U sec.		Co-ordinates at $t = 0·20$ λ/U sec.		Velocity components at $t = 0·20$ λ/U sec.	
	x/λ.	y/λ.	u/U.	v/U.	x/λ.	y/λ.	u/U.	v/U.	x/λ.	y/λ.	u/U.	v/U.
0	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
1	0·13	0·07	0·31	0·11	0·16	0·08	0·32	0·23	0·19	0·10	0·37	0·29
2	0·25	0·10	0·50	0·00	0·30	0·10	0·54	0·18	0·35	0·12	0·72	0·28
3	0·38	0·07	0·31	—0·11	0·41	0·06	0·35	0·04	0·45	0·06	0·61	0·19
4	0·50	0·00	0·00	0·00	0·50	0·00	0·00	0·00	0·50	0·00	0·00	0·00
5	0·62	—0·07	—0·31	0·11	0·59	—0·06	—0·35	—0·04	0·55	0·06	—0·61	—0·19
6	0·75	—0·10	—0·50	0·00	0·70	—0·10	—0·54	—0·18	0·65	0·12	—0·72	—0·28
7	0·87	—0·07	—0·31	—0·11	0·84	—0·08	—0·32	—0·23	0·81	0·10	—0·37	—0·29
8	1·00	0·00	0·00	0·00	1·00	0·00	0·00	0·00	1·00	0·00	0·00	0·00

Vortex No.	Co-ordinates at $t = 0·30$ λ/U sec.		Velocity components at $t = 0·30$ λ/U sec.		Co-ordinates at $t = 0·35$ λ/U sec.		Velocity components at $t = 0·35$ λ/U sec.		Co-ordinates at $t = 0·40$ λ/U sec.		Velocity components at $t = 0·40$ λ/U sec.	
	x/λ.	y/λ.	u/U.	v/U.	x/λ.	y/λ.	u/U.	v/U.	x/λ.	y/λ.	u/U.	v/U.
0	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
1	0·23	0·13	0·47	0·35	0·25	0·15	0·56	0·33	0·28	0·17	0·64	0·33
2	0·42	0·15	0·96	0·26	0·47	0·16	1·07	0·10	0·52	0·16	1·06	—0·04
3	0·51	0·08	0·83	—0·35	0·55	0·06	0·69	—0·68	0·58	0·03	0·30	—0·74
4	0·50	0·00	0·00	0·00	0·50	0·00	0·00	0·00	0·50	0·00	0·00	0·00
5	0·49	—0·08	—0·83	0·35	0·45	—0·06	—0·69	0·68	0·42	—0·03	—0·30	0·74
6	0·58	—0·15	—0·96	—0·26	0·53	—0·16	—1·07	—0·10	0·48	—0·16	—1·06	0·04
7	0·77	—0·13	—0·47	—0·35	0·75	—0·15	—0·56	—0·33	0·72	—0·17	—0·64	—0·33
8	1·00	0·00	—0·00	—0·00	1·00	0·00	0·00	0·00	1·00	0·00	0·00	0·00

Table I.—(continued).

Vortex No.	Co-ordinates at $t = 0\cdot45\ \lambda/U$ sec.		Velocity components at $t = 0\cdot45\ \lambda/U$ sec.		Co-ordinates at $t = 0\cdot50\ \lambda/U$ sec.		Velocity components at $t = 0\cdot50\ \lambda/U$ sec.		Co-ordinates at $t = 0\cdot55\ \lambda/U$ sec.		Velocity components at $t = 0\cdot55\ \lambda/U$ sec.	
	x/λ.	y/λ.	u/U.	v/U.	x/λ.	y/λ.	u/U.	v/U.	x/λ.	y/λ.	u/U.	v/U.
0	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
1	0·31	0·18	0·77	0·34	0·35	0·20	0·90	0·35	0·40	0·22	0·96	0·19
2	0·57	0·16	0·96	—0·27	0·62	0·15	0·81	—0·30	0·66	0·13	0·70	—0·34
3	0·59	—0·01	—0·08	—0·69	0·59	—0·04	—0·29	—0·56	0·57	—0·07	—0·40	—0·32
4	0·50	0·00	0·00	0·00	0·50	0·00	0·00	0·00	0·50	0·00	0·00	0·00
5	0·41	0·01	0·08	0·69	0·41	0·04	0·29	0·56	0·43	0·07	0·40	0·32
6	0·43	—0·16	—0·96	0·27	0·38	—0·15	—0·81	0·30	0·34	—0·13	—0·70	0·34
7	0·69	—0·18	—0·77	—0·34	0·65	—0·20	—0·90	—0·35	0·60	—0·22	—0·96	—0·19
8	1·00	0·00	0·00	0·00	1·00	0·00	0·00	0·00	1·00	0·00	0·00	0·00

Vortex No.	Co-ordinates at $t = 0\cdot60\ \lambda/U$ sec.		Velocity components at $t = 0\cdot60\ \lambda/U$ sec.		Co-ordinates at $t = 0\cdot65\ \lambda/U$ sec.		Velocity components at $t = 0\cdot65\ \lambda/U$ sec.		Co-ordinates at $t = 0\cdot70\ \lambda/U$ sec.		Velocity components at $t = 0\cdot70\ \lambda/U$ sec.	
	x/λ.	y/λ.	u/U.	v/U.	x/λ.	y/λ.	u/U.	v/U.	x/λ.	y/λ.	u/U.	v/U.
0	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
1	0·45	0·26	1·02	0·09	0·50	0·27	1·07	0·01	0·55	0·26	1·11	—0·08
2	0·69	0·10	0·50	—0·60	0·72	0·07	0·26	—0·65	0·73	0·03	—0·06	—0·42
3	0·55	—0·08	—0·53	—0·02	0·51	—0·08	—0·62	0·03	0·48	—0·08	—0·72	0·17
4	0·50	0·00	0·00	0·00	0·50	0·00	0·00	0·00	0·50	0·00	0·00	0·00
5	0·45	0·08	0·53	0·02	0·49	0·08	0·62	—0·03	0·52	0·08	0·72	—0·17
6	0·31	—0·10	—0·50	0·60	0·28	—0·07	—0·26	0·65	0·27	—0·03	0·06	0·42
7	0·55	—0·26	—1·02	—0·09	0·50	—0·27	—1·07	—0·01	0·45	—0·26	—1·11	0·08
8	1·00	0·00	0·00	0·00	1·00	0·00	0·00	0·00	1·00	0·00	0·00	0·00

Table II.—$n = 12$.

Vortex No.	Co-ordinates at $t = 0\cdot00\ \lambda/U$ sec.		Velocity components at $t = 0\cdot00\ \lambda/U$ sec.		Co-ordinates at $t = 0\cdot25\ \lambda/U$ sec.		Velocity components at $t = 0\cdot25\ \lambda/U$ sec.		Co-ordinates at $t = 0\cdot30\ \lambda/U$ sec.		Velocity components at $t = 0\cdot30\ \lambda/U$ sec.	
	x/λ.	y/λ.	u/U.	v/U.	x/λ.	y/λ.	u/U.	v/U.	x/λ.	y/λ.	u/U.	v/U.
0	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
1	0·08	0·05	0·21	0·10	0·13	0·07	0·27	0·22	0·14	0·08	0·29	0·24
2	0·17	0·09	0·43	0·11	0·28	0·12	0·57	0·42	0·31	0·14	0·63	0·48
3	0·25	0·10	0·52	0·00	0·38	0·10	0·82	0·45	0·42	0·12	0·89	0·28
4	0·33	0·09	0·43	—0·11	0·44	0·06	1·07	—0·13	0·49	0·05	1·17	—0·12
5	0·42	0·05	0·21	—0·10	0·47	0·03	0·37	—0·17	0·50	0·02	0·48	—0·28
6	0·50	0·00	0·00	0·00	0·50	0·00	0·00	0·00	0·50	0·00	0·00	0·00
7	0·58	—0·05	—0·21	0·10	0·53	—0·03	—0·37	0·17	0·50	—0·02	—0·48	0·28
8	0·67	—0·09	—0·43	0·11	0·56	—0·06	—1·07	0·13	0·51	—0·05	—1·17	0·12
9	0·75	—0·10	—0·52	0·00	0·62	—0·10	—0·82	—0·45	0·58	—0·12	—0·89	—0·28
10	0·83	—0·09	—0·43	—0·11	0·72	—0·12	—0·57	—0·42	0·69	—0·14	—0·63	—0·48
11	0·92	—0·05	—0·21	—0·10	0·87	—0·07	—0·27	—0·22	0·86	—0·08	—0·29	—0·24
12	1·00	0·00	0·00	0·00	1·00	0·00	0·00	0·00	1·00	0·00	0·00	0·00

Vortex No.	Co-ordinates at $t = 0\cdot35\ \lambda/U$ sec.		Velocity components at $t = 0\cdot35\ \lambda/U$ sec.		Co-ordinates at $t = 0\cdot40\ \lambda/U$ sec.		Velocity components at $t = 0\cdot40\ \lambda/U$ sec.	
	x/λ.	y/λ.	u/U.	v/U.	x/λ.	y/λ.	u/U.	v/U.
0	0·00	0·00	0·00	0·00	0·00	0·00	—	—
1	0·16	0·09	0·30	0·27	0·18	0·11	—	—
2	0·34	0·16	0·71	0·55	0·38	0·19	—	—
3	0·46	0·14	2·05	0·04	0·56	0·14	—	—
4	0·55	0·05	1·34	—0·93	0·58	0·01	—	—
5	0·52	0·01	0·63	—1·72	0·48	—0·02	—	—
6	0·50	0·00	0·00	0·00	0·50	0·00	—	—
7	0·48	—0·01	—0·63	1·72	0·52	0·02	—	—
8	0·45	—0·05	—1·34	0·93	0·42	—0·01	—	—
9	0·54	—0·14	—2·05	—0·04	0·44	—0·14	—	—
10	0·66	—0·16	—0·71	—0·55	0·62	—0·19	—	—
11	0·84	—0·09	—0·30	—0·27	0·82	—0·11	—	—
12	1·00	0·00	0·00	0·00	1·00	0·00	—	—

angular velocity round it. As the surface rolls up, the amplitude of the disturbance increases—in the case considered it is approximately doubled in the time $0\cdot40\ \lambda/\mathrm{U}$ second.

The whole investigation accounts in an approximate theoretical manner for the formation of vortices along the surface, when the surface of discontinuity breaks up owing to instability.

On Dirichlet's Divisor Problem.

By J. R. Wilton, University of Adelaide.

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1. Let $d(n)$ denote the number of divisors of the positive integer n, so that, if

$$n = p_1^{a_1} \dots p_r^{a_r}$$

is the canonical expression of n in prime factors,

$$d(n) = (1 + a_1) \dots (1 + a_r),$$

and let $d(x) = 0$ if x is not an integer; then, if

$$\text{(1.1)} \qquad \mathrm{D}(x) = \sum_{n \leq x}{}' d(n) = \sum_{n \leq x} d(n) - \tfrac{1}{2} d(x),$$

and

$$\text{(1.2)} \qquad \Delta(x) = \mathrm{D}(x) - x \log x - (2\mathrm{C} - 1) x - \tfrac{1}{4},$$

where C is Euler's constant, it was proved by Dirichlet* in 1849 that

$$\text{(1.21)} \qquad \Delta(x) = \mathrm{O}(\sqrt{x}),$$

and more than half-a-century later this result was improved by Voronoï† to

$$\text{(1.22)} \qquad \Delta(x) = \mathrm{O}(x^{\frac{1}{3}} \log x);$$

the most that has yet been proved in this connection is van der Corput's theorem‡

$$\text{(1.23)} \qquad \Delta(x) = \mathrm{O}(x^{27/82} \log^{11/41} x),$$

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* 'Berlin Sitz. Akad. Wiss.,' pp. 69–83 (1849).

† 'J. R. Angew. Math.,' vol. 126, pp. 241–282 (1903).

‡ 'Math. Ann.,' vol. 98, pp. 697–716 (1928).

although there is reason to believe that it may be true that $\Delta(x) = O(x^{\frac{1}{4}+\varepsilon})$ for any $\varepsilon > 0$. I shall assume that

$$\Delta(x) = O(x^{\Theta} \log x); \tag{1.24}$$

for one purpose it will be sufficient to assume the very rough approximation $\Theta < 1$; for another I shall take $\Theta = 1/2$, and for the final step in the proof of theorem 3 I shall use $\Theta = 1/3$, although this is unnecessary, as I show in § 5.

My chief concern in this paper is the derivation of an improved form of a well-known expansion formula for $\Delta(x)$ in a convergent series of Bessel functions, namely

$$\Delta(x) = \sqrt{x} \sum_{n=1}^{\infty} \frac{d(n)}{\sqrt{n}} \mathrm{L}_1 \{4\pi \sqrt{(nx)}\}, \tag{1.3}$$

where $\mathrm{L}_1(z) = -\mathrm{Y}_1(z) - (2/\pi)\mathrm{K}_1(z)$, and Y_1, K_1 are the Bessel functions of the second and third kinds, as defined, for example, in Watson's standard treatise.* The expansion (1.3) was first obtained by Voronoï† in 1904, and was discovered independently by Hardy‡ in 1915; the formula is, moreover, a special case of a much more general theorem proved by Walfisz.§ The most recent proof of (1·3) is contained in a paper by Dixon and Ferrar.|| The methods of all these writers depend upon the theory of functions of a complex variable. A proof by real analysis has been given by Rogosinski,¶ and more recently there has been published by Landau** a characteristically simple and elementary proof by real analysis. Landau proves first another (much easier, because absolutely convergent) expansion formula, also due to Voronoï, namely, if

$$\Delta_1(x) = \int_0^x \Delta(y)dy, \tag{1.41}$$

then

$$\Delta_1(x) = \frac{x}{2\pi} \sum_{n=1}^{\infty} \frac{d(n)}{n} m_2 \{4\pi \sqrt{(nx)}\} \tag{1.42}$$

$$= O(x^{\frac{3}{4}}), \tag{1.43}$$

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* "Theory of Bessel Functions" (Cambridge, 1922), pp. 64 and 78.

† 'Ann. Sci. Ec. Norm. Sup.,' Paris, vol. 21, pp. 207–268 and 459–534 (1904).

‡ 'Proc. Lond. Math. Soc.,' vol. 15, pp. 1–25 (1916). There is an error in the sign of $\mathrm{H}_1 (= 2\mathrm{K}_1/\pi)$ in Hardy's equation (6.33). The error is repeated by Ramanujan in his memoir on "Highly composite numbers" ('Proc. Lond. Math. Soc.,' vol. 14, pp. 347–409 (1915)), and it has escaped the vigilance of the editors of Ramanujan's 'Collected Papers' (Cambridge, 1927).

§ 'Math. Z.,' vol. 22, pp. 153–188 (1925).

|| 'Quart. J. Math.,' vol. 2, p. 31 (1931).

¶ "Neue Anwendung der Pfeifferschen Methode bei Dirichlets Teilerproblem" (Göttingen, 1922).

** 'Math. Ann.,' vol. 97, pp. 251–290 (1927).

where m_2 is defined in (2.11). It is evident from (3.1) that (1.3) is derived by formal differentiation of (1.42), and the whole difficulty of the proof of (1.3) lies in establishing the convergence of the series.

I assume the truth of (1.42), referring to Landau's paper (*loc. cit.*), for a simple proof, and I deduce (1.3) in a form suggested by, and closely resembling, one of Hardy's theorems in the allied theory of the lattice points of a circle. Let $r(n)$ be the number of integral solutions (positive, negative and zero) of the Diophantine equation $y^2 + z^2 = n$, and let

$$\mathrm{R}(x) = \sum_{n \leq x}{}' r(n) = \sum_{n \leq x} r(n) - \tfrac{1}{2} r(x),$$

$$\mathrm{P}(x) = \mathrm{R}(x) - \pi x + 1.$$

[The sum R (x) does not include the term $n = 0$, but P (x) does.]
Then

$$\mathrm{P}(x) = \sqrt{x} \sum_{n=1}^{\infty} \frac{r(n)}{\sqrt{n}} \mathrm{J}_1 \{2\pi \sqrt{(nx)}\}, \tag{1.5}$$

where J_1 is the Bessel function of the first kind, and the series is convergent.* Very accurate information as to the nature of the convergence of the series (1.5) has been obtained by Hardy,† who proves the theorem,

If x and N *are positive, then*

$$\begin{aligned} \mathrm{S}(x, \mathrm{N}) &= \mathrm{P}(x) - \sqrt{x} \sum_{n \leq \mathrm{N}}{}' \frac{r(n)}{\sqrt{n}} \mathrm{J}_1 \{2\pi \sqrt{(nx)}\} \\ &= \mathrm{J}_0 \{2\pi \sqrt{(\mathrm{N}x)}\} - \sqrt{\frac{x}{\mathrm{N}}} \mathrm{P}(\mathrm{N}) \mathrm{J}_1 \{2\pi \sqrt{(\mathrm{N}x)}\} \\ &\qquad + \sqrt{x} \sum_{n=1}^{\infty} \frac{r(n)}{\sqrt{n}} \int_{2\pi\sqrt{(\mathrm{N}x)}}^{\infty} \mathrm{J}_2(t) \mathrm{J}_1\left(t \sqrt{\frac{n}{x}}\right) dt\,; \end{aligned}$$

and, if‡ $x > \mathrm{A}$, $\mathrm{N} > \mathrm{A}$, $\varepsilon > 0$, *then*

$$\mathrm{S}(x, \mathrm{N}) = \mathrm{O}(\mathrm{N}^{-\frac{1}{2}} x^{\frac{1}{2}+\epsilon}) + \mathrm{O}\{(\mathrm{N}x)^{-\frac{1}{4}}\} + \mathrm{O}(x^{\epsilon}).$$

Starting from an integral formula which also is, essentially, due to Hardy§ (although he does not suggest the application here made of it), I prove an analogous theorem for the corresponding series (1.3) by a method which, on the whole, closely follows Hardy's. It is entirely real and elementary; it involves, for instance, no appeal to the properties of the Lebesgue integral. It is evident that the method could be extended to the more general, summable, expansions considered by Oppenheim.*

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* References are given (for example) in my historical paper, 'Messeng. Math.,' vol. 58, p. 67 (1928).

† 'Proc. Roy. Soc.,' A, vol. 107, p. 623 (1925). I have slightly altered Hardy's notation, *ibid.*, vol. 120, p. 369 (1928).

‡ Here, and throughout the paper, A denotes a positive constant, not the same at different occurrences.

§ 'Messeng. Math.,' vol. 57, p. 113 (1927).

So far as I am aware, the only published theorem intermediate between (1.3) and theorem 3 is contained in Oppenheim's paper, the last formula† of which reads, in my notation,

$$(1.6) \qquad \Sigma(x, \mathrm{N}) = \Delta(x) - \sum_{n \leq \mathrm{N}}{}' \sqrt{\frac{x}{n}}\, d(n)\, \mathrm{L}_1\{4\pi\sqrt{(nx)}\} \qquad (x > 0)$$

$$(1.61) \qquad = \mathrm{O}(\mathrm{N}^{-\frac{1}{4}+\epsilon}) \qquad (\epsilon > 0),$$

for large integral N; *if* A $< x <$ A, *and the values of* x *are confined to a set of closed intervals from which the integers are excluded, the* O*-term is uniform.*

2. I employ Hardy's notation (*loc. cit.*, p. 118)

$$(2.1) \quad \mathrm{L}_\nu(z) = -\mathrm{Y}_\nu(z) - (2/\pi)\,\mathrm{K}_\nu(z), \quad \mathrm{M}_\nu(z) = -\mathrm{Y}_\nu(z) + (2/\pi)\,\mathrm{K}_\nu(z),$$

and a modification of it suggested by Dixon and Ferrar,‡ namely (in the particular cases which I require),

$$(2.11) \qquad \begin{cases} l_3(z) = \mathrm{L}_3(z) - 4/\pi z, & l_2(z) = \mathrm{L}_2(z) - 2/\pi, \\ m_2(z) = \mathrm{M}_2(z) - 8/\pi z^2, & l_1(z) = \mathrm{L}_1(z) + (2z/\pi)\log\tfrac{1}{2}z. \end{cases}$$

The theorems which I prove may now be stated as follows.§

THEOREM 1.—*If* $x > 0$, $\mathrm{N} > 0$, *and* $\Sigma(x, \mathrm{N})$ *is defined by* (1.6), *then*

$$(2.2) \qquad \Sigma(x, \mathrm{N}) = \lambda(x, \mathrm{N}) - \Delta(\mathrm{N})\sqrt{(x/\mathrm{N})}\,\mathrm{L}_1\{4\pi\sqrt{(\mathrm{N}x)}\}$$
$$+ \sqrt{x}\sum_{n=1}^{\infty}\frac{d(n)}{\sqrt{n}}\int_{4\pi\sqrt{(\mathrm{N}x)}}^{\infty}\mathrm{L}_2(u)\,\mathrm{L}_1\left(u\sqrt{\frac{n}{x}}\right)du$$

$$(2.21) \qquad = \lambda(x, \mathrm{N}) - \Delta(\mathrm{N})\sqrt{(x/\mathrm{N})}\,\mathrm{L}_1\{4\pi\sqrt{(\mathrm{N}x)}\}$$
$$+ 2\pi\int_{\mathrm{N}}^{\infty}\frac{x}{t}\mathrm{L}_2\{4\pi\sqrt{(xt)}\}\Delta(t)\,dt,$$

where

$$\lambda(x, \mathrm{N}) = \frac{\log \mathrm{N} + 2\mathrm{C}}{2\pi}\mathrm{L}_0\{4\pi\sqrt{(\mathrm{N}x)}\} + \frac{1}{2\pi}\int_{\mathrm{N}}^{\infty}\mathrm{L}_0\{4\pi\sqrt{(xt)}\}\frac{dt}{t}.$$

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* 'Proc. Lond. Math. Soc.,' vol. 26, p. 295 (1927). [I have now completed the work here suggested, and have communicated the results to the London Mathematical Society (August, 1931).]

† *Loc. cit.*, p. 350.

‡ 'Quart. J. Math.,' vol. 1, p. 122 (1930). The lower case letters represent functions which vanish at the origin; to avoid special cases in (3.1) I have slightly changed the definitions of $l_1(z)$ and $l_2(z)$.

§ *Cf.* Hardy (1925), theorems 1, 2 and 3.

THEOREM 2.—*If* $x > 0$, $\mathrm{N} > 0$, *then*

$$(2.3)\qquad \Sigma(x, \mathrm{N}) = \lambda(x, \mathrm{N}) + 2\pi\sqrt{x}\sum_{n=1}^{\infty} d(n) \times \int_{\mathrm{N}}^{\infty} \mathrm{L}_1\{4\pi\sqrt{(xt)}\}\,\mathrm{M}_0\{4\pi\sqrt{(nt)}\}\frac{dt}{\sqrt{t}}.$$

THEOREM 3.—*If* $\mathrm{N} > \mathrm{A}$, $x > 0$, $\mathrm{N}x > \mathrm{A}$, $\varepsilon > 0$, *then*

$$(2.4)\qquad \Sigma(x, \mathrm{N}) = O(x^{\frac{1}{2}+\epsilon}\mathrm{N}^{-\frac{1}{2}}) + O\{(\mathrm{N}x)^{-\frac{1}{4}}\,|\log \mathrm{N}|\} + O(x^{\epsilon});$$

in particular, if $\mathrm{A} < \mathrm{N} < \mathrm{A}x^3$,

$$(2.41)\qquad \Sigma(x, \mathrm{N}) = O(x^{\frac{1}{2}+\epsilon}\mathrm{N}^{-\frac{1}{2}}) + O(x^{\epsilon}).$$

If x is an integer, or if the values of x are confined to a set of closed intervals from which the integers are excluded, there is no error term $O(x^{\epsilon})$ in (2.4) or (2.41).

It is evident that (2.4) includes (1.61), and that $\mathrm{N}^{-\frac{1}{4}+\epsilon}$ may be replaced by $\mathrm{N}^{-\frac{1}{4}}\log \mathrm{N}$ in (1.61). In fact, since the error term $O\{(\mathrm{N}x)^{-\frac{1}{4}}\,|\log \mathrm{N}|\}$ in (2.4) arises solely* from $(\log \mathrm{N})\,\mathrm{L}_0\{4\pi\sqrt{(\mathrm{N}x)}\}$ in (2.2) or (2.3), Oppenheim's formula (1.61) may be improved to

$$(2.42)\qquad \Sigma(x, \mathrm{N}) = \frac{\log \mathrm{N}}{2\pi^2}\,\frac{\cos\{4\pi\sqrt{(nx)} + \frac{1}{4}\pi\}}{(4\mathrm{N}x)^{\frac{1}{4}}} + O(\mathrm{N}^{-\frac{1}{4}}),$$

with the same condition as to uniformity. N need not be an integer, and (2.42) is true for all $x > \mathrm{A}$, if $\mathrm{N} > x^{\kappa}$, where $\kappa > 2$.

Again, in (2.21), $\Delta(\mathrm{N})$ and $\Delta(t)$ may be replaced by $\Delta(\mathrm{N}) + \frac{1}{4}$ and $\Delta(t) + \frac{1}{4}$, respectively, without affecting the truth of the equation. Since $\Delta(t) + \frac{1}{4} \to 0$ as $t \to 0$, we may then make $\mathrm{N} \to 0$ in (2.21) and obtain Hardy's integral equation (*loc. cit.*, 1927) for $\Delta(x)$, namely

$$(2.5)\qquad \frac{\Delta(x) + \frac{1}{4}}{x} = 2\pi\int_0^{\infty}\frac{\Delta(t) + \frac{1}{4}}{t}\,\mathrm{L}_2\{4\pi\sqrt{(xt)}\}\,dt,$$

in which use has been made of the integral

$$(2.6)\qquad \int_0^{\infty}\mathrm{L}_0(z)\frac{dz}{z} = -\tfrac{1}{4}\pi.$$

Proofs of Theorems 1 *and* 2.

3. From the sequence formulæ for Y_ν and K_ν we have

$$(3.1)\qquad \begin{cases} \dfrac{d}{dt}\left\{\left(\dfrac{x}{t}\right)^{\frac{1}{2}n}\genfrac{}{}{0pt}{}{\mathrm{L}_n}{l_n}\right\} = -2\pi\left(\dfrac{x}{t}\right)^{\frac{1}{2}n+\frac{1}{2}}\genfrac{}{}{0pt}{}{\mathrm{L}_{n+1}}{l_{n+1}} \qquad (n = 1, 2), \\[2ex] \dfrac{d}{dt}\left(\dfrac{t}{x}\genfrac{}{}{0pt}{}{\mathrm{M}_2}{m_2}\right) = 2\pi\left(\dfrac{t}{x}\right)^{\frac{1}{2}}\mathrm{L}_1, \qquad \dfrac{d}{dt}\left\{\left(\dfrac{t}{x}\right)^{\frac{1}{2}}\mathrm{L}_1\right\} = 2\pi\mathrm{M}_0, \end{cases}$$

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* That this is so follows from (1.21).

where the argument of each of the functions $M_0, \ldots, L_3$ is $4\pi\sqrt{(xt)}$. I shall also require the definite integrals

$$(3.2) \qquad \int_0^\infty L_1(z)\,dz = 0, \quad \int_0^\infty L_1(z)\log z\,dz = -\tfrac{1}{4}\pi,$$

$$(3.3) \qquad \frac{2\pi x^{3/2}}{n}\int_0^\infty l_3\{4\pi\sqrt{(xt)}\}\,m_2\{4\pi\sqrt{(nt)}\}\frac{dt}{\sqrt{t}} = \begin{cases} 1 & (0 < n < x) \\ \tfrac{1}{2} & (n = x) \\ 0 & (n > x), \end{cases}$$

of which (3.2)—as also (2.6)—may be deduced as limiting cases from formulæ given by Watson (*loc. cit.*, pp. 393 and 388), and (3.3) is derived by integration by parts and use of (3.1) from an integral due to Hardy (*loc. cit.*, 1927 (9.2)), and already referred to, or it may be quoted directly from Dixon and Ferrar (*loc. cit.*, 1930). Hardy's proof is entirely real; that of Dixon and Ferrar appeals to Cauchy's theorem. The discontinuous integral (3.3) is the principal tool in the proof of theorems 1 and 2. From it we deduce, if $N > 0$,

$$(3.4) \qquad D(x) = \sum_{n \leq x}{}' d(n) = 2\pi x^{3/2}\sum_{n=1}^{\infty}\frac{d(n)}{n}\int_0^\infty l_3\{4\pi\sqrt{(xt)}\}\,m_2\{4\pi\sqrt{(nt)}\}\frac{dt}{\sqrt{t}}$$

$$(3.40) \qquad = 2\pi\sum_{n=1}^{\infty} d(n)\int_N^\infty \left(\frac{x}{t}\right)^{3/2} L_3\{4\pi\sqrt{(xt)}\}\frac{t}{n}\,m_2\{4\pi\sqrt{(nt)}\}\,dt$$

$$(3.41) \qquad -4x\int_N^\infty \frac{\Delta_1(t)}{t^2}\,dt + 4\pi^2\int_0^N \left(\frac{x}{t}\right)^{3/2} l_3\{4\pi\sqrt{(xt)}\}\,\Delta_1(t)\,dt$$

$$(3.42) \qquad = 2\pi x\sum_{n=1}^{\infty}\frac{d(n)}{\sqrt{n}}\int_N^\infty L_2\{4\pi\sqrt{(xt)}\}\,L_1\{4\pi\sqrt{(nt)}\}\frac{dt}{\sqrt{t}}$$

$$(3.43) \qquad + 2\pi\int_0^N \frac{x}{t}\,l_2\{4\pi\sqrt{(xt)}\}\{\Delta(t) + \tfrac{1}{4}\}\,dt + 4x\frac{\Delta_1(N)}{N}$$

$$(3.44) \qquad + \tfrac{1}{4}\sqrt{\frac{x}{N}}\,l_1\{4\pi\sqrt{(Nx)}\} + (2C - 1)\,x - 4x\int_N^\infty \frac{\Delta_1(t)}{t^2}\,dt,$$

on integrating by parts. The change of order in either part of (3.41) is obviously justifiable.

In (3.43) we substitute for $\Delta(t)$ its value as given by (1.2), and employ (2.11) and (3.1); after a simple reduction, we obtain, for the sum of (3.43) and (3.44),

$$x(\log x + 2C - 1 + 4\beta)$$

$$(3.45) \qquad -2\pi x\int_0^N (\log t + 2C - 1)\,L_2\{4\pi\sqrt{(xt)}\}\,dt + \tfrac{1}{4}\sqrt{\frac{x}{N}}\,L_1\{4\pi\sqrt{(Nx)}\}$$

$$(3.46) \qquad + 2\pi\int_1^N \frac{x}{t}\,L_2\{4\pi\sqrt{(xt)}\}\,D(t)\,dt,$$

where*

$$(3.47)\qquad \beta = \tfrac{1}{2}\log 2\pi + C - \tfrac{3}{2} - \int_1^\infty \frac{\Delta_1(t)}{t^2}\,dt.$$

If, omitting the argument $4\pi\sqrt{(xt)}$ of the L functions, we observe that

$$\frac{d}{dt}\left\{t(\log t + 2C - 1)\sqrt{\frac{x}{t}}L_1\right\}$$
$$= (\log t + 2C)\sqrt{\frac{x}{t}}L_1 - 2\pi x(\log t + 2C - 1)L_2,$$

and employ (3.2), we find that (3.45) is equal to

$$(3.48)\qquad \tfrac{1}{4} + \{D(N) - \Delta(N)\}\sqrt{\frac{x}{N}}L_1\{4\pi\sqrt{(Nx)}\}$$
$$+ \int_N^\infty (\log t + 2C)\sqrt{\frac{x}{t}}L_1\,dt;$$

and it is readily verified that (3.46) is equal to

$$(3.49)\qquad \sum_{n\leq N}{}' d(n)\sqrt{\frac{x}{n}}L_1\{4\pi\sqrt{(nx)}\} - D(N)\sqrt{\frac{x}{N}}L_1\{4\pi\sqrt{(Nx)}\}.$$

Making an obvious change of variable in (3.42) and collecting results, we have the first part of theorem 1, except that, on the right of (2.2), there is an extra term $4\beta x$. It will appear that β vanishes, although the proof which I give is very indirect. Assuming, for the moment, that $\beta = 0$ and that (1.3) has been established, we shall have theorem 2 on integrating (3.42) by parts; in particular theorem 2 will follow when (2.4) or (2.2) is proved. And the second part of theorem 1 will be proved when it is shown that (3.40) is equal to

$$(3.5)\qquad 4\pi^2\int_N^\infty \left(\frac{x}{t}\right)^{3/2} L_3\{4\pi\sqrt{(xt)}\}\,\Delta_1(t)\,dt,$$

for integration by parts will then yield the integral on the right of (2.21) in place of (3.42). To establish the change of order of integration and summation

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* It is an unsatisfactory feature of the analysis that the troublesome term $4\beta x$ is artificially introduced for the pleasure of proving that it vanishes. It arises from the use of the function l_3, instead of L_3, in (3.4); but this appears to be essential, for the integral with L_3 diverges at the origin. On account of the presence of the term $4\beta x$ I have to prove theorem 3 before being able to complete the proofs of theorems 1 and 2. It adds nothing to the total length of the proof. A direct proof that $\beta = 0$ may be derived in a couple of lines from a formula given by Oppenheim (*loc. cit.*, p. 342 (9·4)), namely

$$(\alpha)\ \int_1^x \frac{D(u)}{u}\,du = \sum_{n\leq x} d(n)\log\frac{x}{n} = (x + \tfrac{1}{4})\log x - 2(1 - C)x$$
$$+ \tfrac{1}{2}\log 2\pi - \frac{1}{2\pi}\sum_{n=1}^\infty \frac{d(n)}{n}L_0\{4\pi\sqrt{(nx)}\};$$

but the proof of this involves Cauchy's theorem—in a quite simple way, it is true, if (α) is all that is required—and I prefer to regard (α) as resulting by integration from (1.3), the value of the constant being determined by the fact that $\beta = 0$.

involved in the equality of (3.40) and (3.5) it is clearly sufficient to prove that (3.42) tends to zero as $N \to \infty$. That this is so will appear in the course of the proof of theorem 3.

Proof of Theorem 3.

4. For the proof of the remaining theorem I require a lemma which (except that the Bessel functions J_1, J_2 are replaced by L_1, L_2) is, both in statement and proof, a transcription of one of Hardy's.*

LEMMA.—*If* $\tau > A$, $y > A$, *and* $J(y) = \int_\tau^\infty L_2(u) L_1(yu)\, du$, *then*

$$J(y) = \frac{\operatorname{sgn}(1-y)}{\pi y^{3/2}} \int_{|1-y|\tau}^\infty \frac{\sin u}{u}\, du + O\left(\frac{1}{\tau y^{3/2}}\right). \tag{4.11}$$

If $\tau > A$, $y > 1 + A$, *then*

$$J(y) = O(\tau^{-1} y^{-3/2}). \tag{4.12}$$

And, if $0 < y < 1 - A$, $\tau y > A$, *then*

$$J(y) = O(\tau^{-1} y^{-\frac{1}{2}}). \tag{4.13}$$

We have to apply the lemma to the series on the right of (2.2), so that

$$\tau = 4\pi \sqrt{(Nx)}, \qquad y = \sqrt{(n/x)},$$

and we suppose that the conditions of theorem 3 are satisfied.

Let ξ be the integer such that

$$x - \tfrac{1}{2} \leq \xi < x + \tfrac{1}{2} \quad (x > \tfrac{1}{2}), \tag{4.20}$$

and let

$$\Xi = \frac{\operatorname{sgn}(x-\xi)}{\pi} \left(\frac{x}{\xi}\right)^{5/4} d(\xi) \int_{4\pi\sqrt{N}\,|\sqrt{x}-\sqrt{\xi}|}^\infty \frac{\sin u}{u}\, du, \tag{4.21}$$

so that

$$\Xi = 0, \text{ if } x = \xi, \quad |\Xi| < A d(\xi), \text{ in any case,} \tag{4.22}$$

and, if $|x - \xi| > A$,

$$|\Xi| < A d(\xi) x^{\frac{1}{2}} N^{-\frac{1}{2}} = O(x^{\frac{1}{2}+\epsilon} N^{-\frac{1}{2}}) \qquad (\varepsilon > 0). \tag{4.23}$$

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* Hardy (1925), p. 629, lemma 2. The last part of the proof as given on p. 629 is wrong; *vide* the correction in 'Proc. Roy. Soc.,' A, vol. 120, p. 369 (1928).

If $x \leqslant \frac{1}{2}$, let $\Xi = 0$. Then, by (4.13), (4.11) and (4.12),

$$\left| \sqrt{x} \sum_{n=1}^{\infty} \frac{d(n)}{\sqrt{n}} \int_{4\pi\sqrt{(Nx)}}^{\infty} L_2(u) L_1\left(u \sqrt{\frac{n}{x}}\right) du - \Xi \right|$$

$$(4.24) \qquad < A\sqrt{x} \sum_{1 \leq n < (1-A)x} \frac{d(n)}{\sqrt{n}} (Nx)^{-\frac{1}{4}} \left(\frac{x}{n}\right)^{\frac{1}{4}}$$

$$(4.25) \qquad + \frac{A\sqrt{x}}{\sqrt{N}} \left\{ \sum_{Ax < n < \xi} \frac{d(n)}{\sqrt{n}(\sqrt{x} - \sqrt{n})} + \sum_{\xi < n < Ax} \frac{d(n)}{\sqrt{n}(\sqrt{n} - \sqrt{x})} \right\}$$

$$(4.26) \qquad + A\sqrt{x} \sum_{n > Ax} \frac{d(n)}{\sqrt{n}} (Nx)^{-\frac{1}{4}} \left(\frac{x}{n}\right)^{\frac{1}{4}}.$$

[(4.24) and (4.25) are null if $x \leqslant 3/2$.]

It is readily seen, by partial summation, that (4.24) and (4.26) are both $< AN^{-\frac{1}{4}} x^{\frac{1}{4}} |\log x|$. As regards (4.25), it is, on account of (4.20),

$$(4.27) \qquad < \frac{A\sqrt{x}}{\sqrt{N}} \left\{ \operatorname*{Max}_{Ax < n < Ax} d(n) \right\} \sum_{n < Ax} \frac{1}{n} = O(x^{\frac{1}{4}+\epsilon} N^{-\frac{1}{2}}).$$

Thus

$$(4.28) \qquad (3.42) = \Xi + O(x^{\frac{1}{4}+\epsilon} N^{-\frac{1}{2}}),$$

and since $\Xi \to 0$ as $N \to \infty$ [although not uniformly for values of x in the interval $(\xi - \varepsilon, \xi + \varepsilon)$], it follows that (3.42) tends to zero as $N \to \infty$, and theorems 1 and 2 will be proved when it has been shown that $\beta = 0$.

In (2.2) it is evident that

$$\lambda(x, N) = O\{(Nx)^{-\frac{1}{4}} |\log N|\},$$

and the second term on the right is, by (1.24),

$$(4.3) \qquad O(x^{\frac{1}{4}} N^{\Theta - \frac{3}{4}} |\log N|).$$

It has thus been proved that

$$(4.4) \quad \Sigma(x, N) = 4\beta x + O(x^{\frac{1}{4}+\epsilon} N^{-\frac{1}{2}}) + O\{(Nx)^{-\frac{1}{4}} |\log N|\}$$
$$+ O(x^{\epsilon}) + O(x^{\frac{1}{4}} N^{\Theta - \frac{3}{4}} |\log N|).$$

But assuming only the trivial result that $\Theta < 1$, and taking $N = \frac{1}{2}$, $\varepsilon = \frac{1}{4}$ in (4.4), we have, if $x > A$,

$$4\beta x = \Delta(x) + O(x^{\frac{1}{2}})$$
$$= O(x^{\Theta} \log x) + O(x^{\frac{1}{2}}) = o(x).$$

Hence $\beta = 0$.

If we assume Voronoï's theorem, that $\Theta \leqslant \frac{1}{3}$, then (4.3) is included in the first term on the right of (2.4) if $A < N < Ax^3$, and it is included in the second term if $N > Ax^3$. The three theorems are thus established.

It has been assumed that $d(n) = O(n^\epsilon)$; if we make use of Wigert's result* as to the maximum order of $d(n)$, namely,

$$d(n) < 2^{(1+\epsilon)\log n/\log\log n} \qquad [\epsilon > 0,\ n > n_0(\epsilon)],$$

we may replace x^ϵ in (4.23) and (4.27), and therefore also in (2.4) and (2.41) by

$$2^{(1+\epsilon)\log x/\log\log x} \qquad (\epsilon > 0,\ x > e),$$

and by unity if $x < A$. The consequent improvement in theorem 3 is, however, of little or no significance.

If $x \geqslant 1$, and we choose $N \geqslant x^{1+\delta}$ $(\delta > 0)$ and $\epsilon < \frac{1}{2}\delta$, we have, uniformly with respect to x,

$$\Sigma(x, N) = \Xi + o(1), \tag{4.5}$$

as $N \to \infty$, where Ξ is given by (4.21). Thus Ξ exhibits the Gibbs phenomenon of the series (1.3).

5. The inequality $\Theta \leqslant \frac{1}{3}$ lies less deep† than (1.3), so that there is no objection to quoting it in the proof of theorem 3. It is however, unnecessary to do so, for if, in (4.4), we put $\beta = 0$, and take $\Theta = 1$, $N = x^{\frac{1}{3}}$, $x > A$, we have

$$\Sigma(x, x^{\frac{1}{3}}) = O(x^{\frac{1}{3}+\epsilon}); \tag{5.1}$$

and since, from the asymptotic expansion of the Bessel functions,

$$L_1\{4\pi\sqrt{(nx)}\} = \frac{2}{\pi}\,\frac{\cos\{4\pi\sqrt{(nx)} - \frac{1}{4}\pi\}}{(4nx)^{\frac{1}{4}}} + O\left\{\frac{1}{(nx)^{\frac{3}{4}}}\right\}, \tag{5.11}$$

it follows from (1.6) and (5.1) that

$$\Delta(x) = O(x^{\frac{1}{3}+\epsilon}),$$

and, therefore, instead of (4.3), we may write

$$O(x^{1/4}\,N^{-(5/12)+\delta}) \qquad (\delta > 0). \tag{5·2}$$

Given $\eta > 0$, choose

$$\delta < 1/12, \qquad \delta < \eta/9;$$

then it is easily verified that (5.2) is

$$O(x^{\frac{1}{2}+\eta}N^{-\frac{1}{2}}) \quad \text{if} \quad N < x^{3+36\delta}, \quad \text{and} \quad O\{(Nx)^{-\frac{1}{4}}\} \quad \text{if} \quad N > x^{3+36\delta}.$$

This completes the proof of theorem 3 without having recourse to (1.22).

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* 'Arkiv Mat.,' vol. 3, No. 18 (1906).

† See, for example, Landau (1927).

Again, by one of Landau's lemmas (*loc. cit.*, Satz 28) we have from (2.41) and (5.11), if $A < N < Ax$,

$$\Delta(x) = O(x^{21/80+\epsilon} N^{1/5}) + O(x^{1/2+\epsilon} N^{-1/2}),$$

and, if we put $N = x^{19/56}$, we obtain

$$\Delta(x) = O(x^{37/112+\epsilon}), \tag{5.3}$$

where $37/112 + \varepsilon < 1/3$, if $\varepsilon < 1/336$.

[Of course the difficulty in the proof of (5.3) lies precisely in the proof of the lemma which I have quoted.]

Electron Scattering in Helium.

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Scattering of electrons in helium has been carefully investigated by (among others) Kollath,* who measured the scattering at electron velocities corresponding to 1 to 40 volts. To test the formula for scattering, which Mott† has deduced by means of Born's method, it was of interest, as was also emphasised by the work of Møller,‡ to get measurements at higher velocities. Earlier measurements, *e.g.*, those by Dymond and Watson§ and by McMillen|| have given the scattering as a function of the angle of scattering. In the present paper are given the results for scattering at a fixed angle of 90° and for different electron velocities corresponding to from 40 to 300 volts.

The measurements were carried out with an arrangement, of which the principal part is shown schematically in fig. 1. From the heated tungsten filament G, which had a potential —V volts relatively to the tube H, an electron beam of small circular section passed through H into the upper tube R. During

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* 'Ann. Phys.,' vol. 87, p. 259 (1928).

† 'Proc. Camb. Phil. Soc.,' vol. 25, p. 304 (1929); 'Proc. Roy. Soc.,' A, vol. 127, p. 658 (1930), cited as Mott I and Mott II, respectively.

‡ 'Z. Phys.,' vol. 66, p. 513 (1930).

§ 'Proc. Roy. Soc.,' A, vol. 122, p. 571 (1929).

|| 'Phys. Rev.,' vol. 36, p. 1034 (1930).

the experiment, H and R were kept at the same potential. Electrons, which at 0 are deflected through 90°, will pass through a ring-slit S_{II} and another ring-slit into the Faraday-chamber E_{II}, where the amount of electrons is measured by a Lindeman electrometer connected to the chamber. The direct beam of electrons hits the small circular hole S_{I}, through which the electrons pass into the Faraday-chamber E_{I}. E_{I} is connected to a second Lindeman electrometer, which permits a measurement of the direct beam.

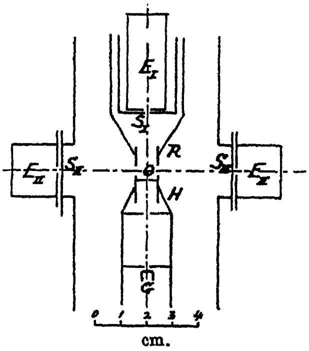

FIG. 1.

In the present investigation the elastic impacts only are measured. The potential at E_{II}—in the following denoted by P—was always negative relatively to the tubes R–H, and ions, which were formed at 0, could eventually be attracted by E_{II} and give a false measurement of the deflected electrons. To avoid this the metal screen with the ring-slit S_{II} was put between O and E_{II}. When S_{II} had a small positive potential relatively to R–H, the positive ions were repulsed, and as the energy of the ions in question was only small, a small potential (2–16 volts) was quite sufficient to stop them.

The slit S_{II} was less wide than the slit in E_{II}. In this way it was made certain that all the electrons passing S_{II} reached the interior of E_{II}. In the first measurements large openings covered with nets of fine metal wire were used, but the electrostatic screening of the nets was not effective at the higher potentials, and measurements therefore were not possible. By using narrow slits this difficulty was avoided. As a control the scattering was measured first with the width of S_{II} equal to 1·0 mm. and then equal to 0·5 mm., and exactly half the scattering was found in the latter case. The slit in E_{II} was in both cases 1·0 mm. wider than the slit S_{II}. The apparatus was built in such a way that these widths and other important dimensions could be determined with an accuracy of more than 0·1 mm., and the electron beam could be centred exactly.

In front of E_{I} the circular opening S_{I} was arranged to allow a well-defined measurement of the direct electron beam. The diameter of S_{I} was 2 mm. and of the opening in E_{I} 3 mm. When S_{I} was put at the same potential as S_{II}, and E_{I} about the same potential as E_{II}, the direct beam would pass through about the same electric fields as the deflected beam.

The length of the part of the electron beam from which the scattering was measured could be determined with accuracy by measuring the distance between H and R. All the metal parts were of copper, covered with a thin layer of lamp black. As insulating material compressed amber (Ambroïn) was used. With the pump continuously running, the apparatus could be evacuated to a pressure of about $5 . 10^{-5}$ mm. Hg. The pressure in the apparatus was measured by means of a MacLeod manometer, which could be controlled by an ionisation gauge.

To determine the scattering the charges on E_I and E_{II} were measured on the two electrometers, after the filament G had been heated for a short time (5 to 30 seconds), and accordingly electrons sent through the apparatus. The charges at E_I could be determined, when the volt-sensitivity of the electrometer (usually 200 scale divisions per volt) and the capacity was known. This capacity was varied within wide limits by means of a precision condenser (from $0 \cdot 01$ μ F to 3 μ F). The charge at E_{II}, the capacity of which was kept as small as possible (about 100 cm.), was determined directly, by means of a Harms' condenser, connected permanently to E_{II} and the electrometer. The charge-sensitivity could thus always be controlled, and was mostly kept at 10 scale divisions, [$= 0 \cdot 016$ electrostatic units]. In the following all measurements will be given expressed in scale divisions on electrometer E_{II}, when E_I from the direct electron beam had received such a charge (300 e.s. units) that its potential had changed $0 \cdot 100$ volt at a value of its capacity equal to $1 \cdot 00$ μ F. Measurements at other capacity values have been reduced so as to correspond to this value. $1 \cdot 0$ sc. E_{II} thus means that E_{II} has received an electron amount, which is $5 \cdot 3 . 10^{-3}$ per cent. of the amount reaching E_I.

The accelerating potential, V volts, was measured at a voltmeter connected to the filament G and the tube H. The velocity of the deflected electrons could be determined in the retarding field between S_{II} and E_{II}. The potential difference, M volts, between E_{II} and G was read on a second voltmeter. Some typical retarding potential curves are shown in fig. 2. The volt scale on the abscissa axis is double, the lower scale gives the potential difference M volts between the filament and E_{II}, while the upper gives the potential difference P volts between the tubes H–R and E_{II}, and accordingly the velocity of the deflected electrons measured in E_{II}. The ordinate gives in scale divisions the amount of electrons reaching E_{II}. The steep fall in the curves shows that the velocity of the deflected electrons can be determined with more than 1 volt accuracy. The nearly horizontal run of the curves is the proof that practically all the deflected electrons have the same velocity.

Even at the highest vacuum obtained in the apparatus there will be a residual scattering on account of the traces of gases left in the apparatus. It is therefore necessary to measure the scattering at the best possible vacuum. This gives

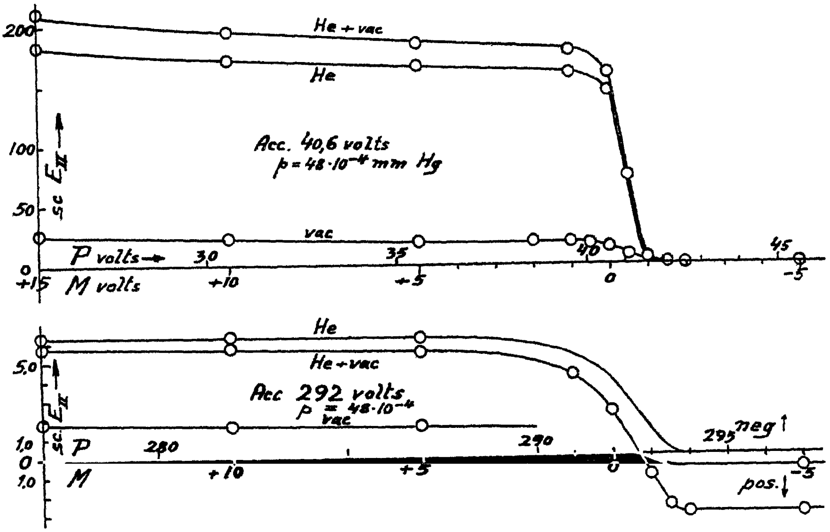

FIG. 2.

the curves marked with " vac." By subtracting these curves from the curves obtained in helium at a pressure of p mm. Hg (marked He + vac), the retarding potential curves in pure helium (marked He) are obtained. The horizontal part of the He-curve gives a control of the purity of the helium gas. Even small amounts of air as an impurity in the helium will cause a steeper slope of this part of the curve.

Considering the curves obtained with large accelerating potential, it will be remarked that at large values of the retarding potential the current to E_{II} has the opposite direction. This current, which is quite constant at the larger retarding potentials, depends very much on the pressure p and increases with p^2. At lower accelerating potentials this current is negligible, at voltages between 100–150 volts it begins to show itself, and at still higher voltages it is constant. This current can be explained by assuming that in the space between S_{II} and E_{II}, as the result of short wave radiation coming from the region O in the apparatus, positive ions are formed, and that these ions are drawn into E_{II} by the retarding field. The true retarding potential curve is then constructed as shown in the figure. From the (He + vac)-curve the (vac)-curve is subtracted, and the resulting curve (He) shifted so that the horizontal part at larger retarding potentials coincides with the abscissa axis.

It appears from fig. 2 that the difference between measurements at M = + 10 volts and at M = — 5 volts will give a good determination of the elastically reflected amount of electrons.

The potential of electrode E_I is at the time of measurement 10 volts less than the accelerating potential. In this way, in the direct beam, only electrons which have lost no energy are measured. Retarding potential curves obtained at E_I in the direct beam, are of the same type and appearance as the curves shown for the deflected beam in fig. 2. Control measurements show that one gets a reliable measurement of the direct electron beam in this way. Only at higher currents together with low tensions, *e.g.*, a current from G to H of more than 0·1 mA. and 40 volts accelerating potential, can space charges between S_I and E_I cause much disturbance. Their appearance is easily detected, and in the later experiments they are completely avoided.

The helium gas was purified through charcoal cooled in liquid air, and was passed through the apparatus with a constant velocity during the experiment.

In fig. 3 is shown how the scattering depends on the pressure p. As ordinate the current to E_{II} in scale divisions, as abscissa the pressure in millimetres Hg. It will be seen that the scattering is a linear function of the pressure, which in the different experiments are shown to hold for pressures below $p = 100 \, . \, 10^{-4}$

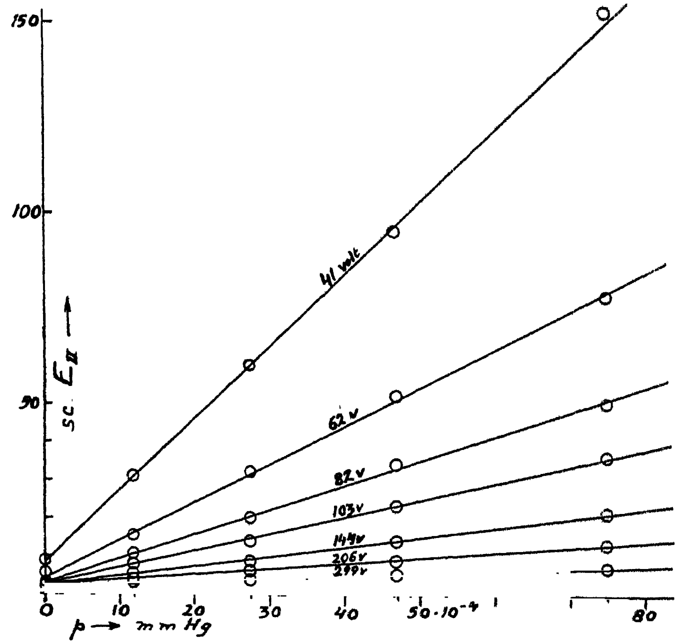

FIG. 3.

mm. Hg. At higher pressures the scattering between H–R and E_{II} wil show itself. The observations were always made on the rectilinear part of these curves. The vacuum value extrapolated from the curve is always in good agreement with the direct measured value for the scattering in vacuum.

From a series of observations, as in fig. 3, one can determine for different potentials the amount of the scattering at a certain pressure, *e.g.*, $p = 1 \cdot 0 \,.\, 10^{-4}$ mm. Hg by dividing the scattering by $p \,.\, 10^4$ after having corrected for the vacuum scattering. As a mean value for this scattering determined from seven reliable series of observations, each containing measurements of scattering at various pressures between $7 \,.\, 10^{-4}$ mm. and $105 \,.\, 10^{-4}$ mm., the following table may be given.

Table I.—Relative Scattering at 90°.

I.	II.	I.	II.
volts	sc. E_{II}	volts	sc. E_{II}
42	3·78	143	0·54
51	2·62*	204	0·29
62	2·04	246	0·19
81	1·26	296	0·14
102	0·90		

* Only determined from a single series of observations.

In column I is given the accelerating potential; in column II the relative scattering, measured in scale divisions at E_{II} divided by the pressure $p \,.\, 10^4$, as previously mentioned. Fig. 4 shows the corresponding scattering curve.

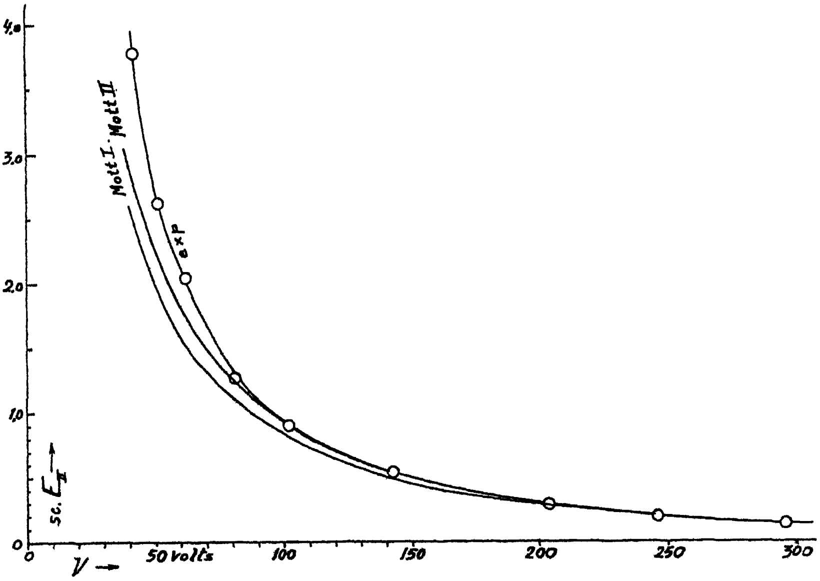

Fig. 4.

The mean value given in the table needs the following explanation. The first experiments were all made with exactly the same apparatus, but the absolute values for the scattering were not the same in the different experiments. The relative scattering was, however, always the same, as the different scattering curves could be made to coincide, if the different series of observations were multiplied by different factors, which varied between 1·0 and 0·64 for the different series. The cause of this was a poor centring of the electron beam. In these experiments the holes in the tube H, through which the electron beam passed, were 2 mm. in diameter. The holes in S_I and E_I were also 2 mm. in diameter. Even a small shift of S_I and E_I relatively to the electron beam would therefore change the amount of electrons, which reaches E_I, very considerably. To avoid this, the holes in H were made larger (diameter about 4 mm.), so that the electron beam was of a diameter much larger than the holes in S_I and E_I. Furthermore, the apparatus was made so that the centring could be made visually with great accuracy. After this improvement two series of observations made on two different days gave the same absolute scattering. The scattering at *e.g.* 62, 81 and 102 volts gave in one series the values, 2·02, 1·15 and 0·90 sc. E_{II}, and in another series the values, 2·08, 1·25 and 0·89 sc. In these measurements E_I does not measure the total direct electron beam, but only a certain small fraction thereof. Since in this case less electrons pass through the hole S_I, the above-mentioned difficulty with the space charge will disappear.

In the different series of observations with an electron beam of a diameter 2 mm. and of diameter 4·5 mm., the relative scattering was found to be the same. In the first experiments the distance between H and R, the length of the scattered beam, was 13 mm.; later this distance was diminished to 5·2 mm. The distance from H to S_{II} was 29 mm.; the scattering was therefore observed between the two angles $\theta = 90° + 12\frac{1}{2}°$ and $90° - 12\frac{1}{2}°$ in the first experiments, and in the later experiments between $\theta = 90° \pm 6°$. Since the scattering in these two angular intervals is found to be the same, and as the theoretical curves of Mott also show that the scattering varies almost linearly with varying scattering angle, no attempt was made to determine the scattering within a smaller angle interval. The relative scattering curve has, as will be understood, been measured under several different experimental conditions, which should prove the reliability of the observations.

As mentioned before, Mott has published two papers about the scattering (*loc. cit.*). In the first (Mott I) he gives sufficient data for calculating the scattering. By using his table and making the theoretical curve coincide with the experimental curve at high velocities the curve marked Mott I in fig. 4 can be obtained. It will be seen that the experimental curve gives a much larger scattering at low velocities than the theoretical one. The deviations at small velocities were also to be expected from the remarks which Møller (*loc. cit.*) makes in the end of his work, and also from remarks of Mott himself.

Better agreement will be found by means of the calculations in Mott's second paper, where the scattering is expressed by the following formula

$$I_\theta = \frac{e^4}{4m^2v^4 \sin^4 \frac{1}{2}\theta}(Z - F)^2, \tag{1}$$

where I_θ is " scattered intensity," the total scattered number is then

$$2\pi \int_0^\pi I_\theta \sin \theta \, d\theta.$$

e, m and v the charge, mass and velocity of the electron, θ the angle of scattering, Z the charge of the nucleus and F is the atomic form factor, a function of $1/\lambda \sin \frac{1}{2}\theta$, where λ is the wave-length of the electron beam. Expressed by the accelerating potential difference V, we get

$$I_\theta = \left(\frac{e}{4V}\right)^2 \frac{(Z - F)^2}{\sin^4 \frac{1}{2}\theta}. \tag{2}$$

At $F = 0$ this formula is the same as Rutherford's formula for the scattering of a heavy nucleus. For details the reader is referred to Mott's paper.*

If a series of values for F, calculated by R. W. James, using Hartree's atomic field, and kindly communicated to the author by Mott, is inserted in formula (2), one gets the curve marked Mott II. This curve is, as before, made to coincide with the experimental curve at the higher potentials. It will be noticed how well the theoretical curve follows the experimental at potentials above 100 volts. On the other hand, the deviations at low potentials are still present. The reason why better agreement is found between experiment and the curve " Mott II " is that, although the formulæ in the two papers by Mott are essentially the same, the better value of F, calculated by James, is used in the curve " Mott II."

From formula (2) it appears that in a representation of the scattering as a function of $1/V^2$, the curve for scattering by the nucleus ($F = 0$) will be a straight line, reaching the abscissa axis at $1/V^2 = 0$ or $V = \infty$. In fig. 5 the experimental scattering is shown as a function of $1/V^2$; the corresponding values of V are also given on the lower scale at the abscissa axis, the ordinates being the same as in fig. 4.

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* See also H. Bethe, 'Ann. Physik,' vol. 5, p. 383 (1930).

The larger experimental scattering at low potentials and the agreement between theory and experiments at high potentials will clearly be seen. The

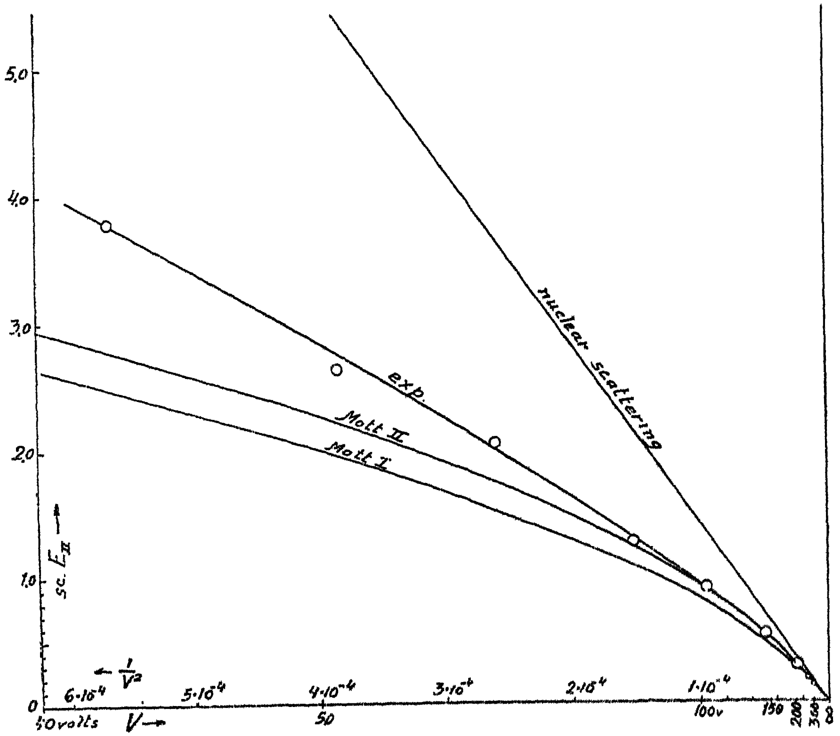

FIG. 5.

curve "nuclear scattering" corresponds to curve Mott II, when F = 0. As the nuclear scattering is a straight line in the figure, one may conclude that, within the limits of experimental error, the scattering is nuclear above 200 volts.

The work is being continued.

The author wishes to express his thanks to Professor Niels Bohr for his kind interest in the work, and to the trustees for the "Carlsbergfond" for grants during the work.

Summary.

The scattering of electrons of velocities corresponding to 40–300 volts in helium at low pressures through the scattering angle θ = 90° has been measured. Table I gives the relative scattering. Figs. 4 and 5 give the experimental scattering curve compared with the theoretical formula of Mott. Agreement is found above 100 volts; below this potential the experimental scattering is larger than the theoretical.

The Kinetics of the Decomposition, in Carbon Tetrachloride Solution, of Ozone and of Ozone-Chlorine Mixtures.

By E. J. BOWEN, E. A. MOELWYN-HUGHES, and C. N. HINSHELWOOD, F.R.S.

(Received July 8, 1931.)

It was recently found that the decomposition of chlorine monoxide takes place at the same rate in solution in carbon tetrachloride as in the gaseous state.* Under both conditions the reaction occurs in consecutive stages, each bimolecular. The rate of the unimolecular decomposition of nitrogen pentoxide is also uninfluenced by carbon tetrachloride. Thus this solvent appears to be established as a "normal" medium for reactions of varying kinetic type. The interest of this lies in the fact that with reactions that cannot be measured in the gaseous state at all, the rate in carbon tetrachloride can be taken as the rate which the reaction would have in the absence of a medium, and the influence of any given solvent can at once be recognised as accelerating or retarding. In this way it may be possible to obtain a deeper understanding of the effect of solvents on the rates of chemical reactions.

In the meantime it is desirable to make as many direct measurements as possible on reactions which can be measured both in the gas and in solution. This paper deals with the decomposition of ozone, and with the catalytic decomposition of ozone by chlorine, both in carbon tetrachloride solution. The gaseous reactions have both been fairly extensively studied.† The catalytic reaction takes place in the dark in a complex series of changes, and has even been said, though on somewhat uncertain evidence, to involve chains of 10^4 cycles; nevertheless, the rate in carbon tetrachloride solution is the same as the rate in the gas phase within a factor of 1·5 to 1. Further, in the corresponding photochemical reaction the number of molecules of ozone decomposed for each quantum of light is 2 both in the gas and in solution. Thus we have evidence that the several different chemical changes involved in these reactions are all almost unaffected by the carbon tetrachloride.

On the other hand, the decomposition of ozone alone takes place much more rapidly in carbon tetrachloride than in the gas. But it becomes unimolecular instead of bimolecular; thus we have not a mere change in rate, but a considerable modification of the reaction mechanism. The cause of this interesting phenomenon is discussed later, and it becomes obvious that special circumstances come into play. When these are taken into consideration, the conclusion that carbon tetrachloride may be regarded as a "normal" solvent is not weakened.

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* Moelwyn-Hughes and Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 131, p. 177 (1931).

† Wulf and Tolman, 'J. Amer. Chem. Soc.,' vol. 49, p. 1650 (1927); Bodenstein, Padelt and Schumacher, 'Z. Phys. Chem.,' B, vol. 5, p. 209 (1929).

Experimental Procedure.

The solution of ozone in carbon tetrachloride was prepared as follows: a Siemens ozoniser was connected by means of a ground-glass joint to a 500 c.c. separating funnel, which was fitted with an outlet tube and an auxiliary dropping funnel. Before starting an experiment the taps and joints were moistened with carbon tetrachloride, and a metal tube prolonging the glass outlet was heated so as to decompose any escaping ozone. 300 c.c. of the pure solvent were poured into the vessel, and a slow current of ozonised oxygen was allowed to bubble through the liquid until it took on a sky-blue colour. At this stage a known volume—usually a few cubic centimetres—of a stock solution of pure dry chlorine in carbon tetrachloride was introduced through the dropping funnel, and washed through with 10 c.c. of the pure solvent. To ensure complete mixing, a rather more agitated stream of ozonised oxygen was led through the liquid for a few seconds, the rate of flow being then reduced so as just to maintain the concentration of ozone constant. Rejecting the first and last samples, the solution was delivered into 10 calibrated reaction tubes, of about 25 c.c. volume and with long stems. These were sealed off, placed in a dark thermostat for a measured time, and then chilled in ice. The free space in the sealed tubes was as small as safety permitted, *i.e.*, about 0·5 c.c. or less. The amount of ozone present in each sample was estimated by pouring the solution into an excess of neutral potassium iodide solution, adding a measured excess of acid, and titrating first with N/100 sodium thiosulphate and then with N/100 baryta using phenol-phthalein as indicator

$$O_3 + 2H^+ + 2I^- = O_2 + H_2O + I_2.$$

The colour of the solution of iodine in carbon tetrachloride is intense enough to allow one to dispense with the use of starch. The number of cubic centimetres of *acid* required by any sample should, of course, be the same as the number of cubic centimetres of sodium thiosulphate. For samples of carbon tetrachloride containing both ozone and chlorine, the procedure was just the same; here, the acid titre (T_a) gives the concentration of ozone, and the difference ($T_{\text{thio.}} - T_a$) between the sodium thiosulphate and the acid titres gives the concentration of chlorine. Alternatively, the concentration of chlorine may be calculated directly from that of the stock solution.

The Decomposition of Ozone alone in Carbon Tetrachloride Solution.

The carbon tetrachloride used throughout this investigation was a specially purified preparation, guaranteed by Messrs. Albright & Wilson, Ltd., to be free from sulphur and chlorine. About 50 tubes were filled with solutions of ozone, of various known concentrations, and were kept in the thermostat for different intervals. On plotting the percentage change undergone by these samples against the time, it was found that ozone dissolved in carbon tetrachloride decomposes unimolecularly, k_1 at 71·0° C. being $1\cdot22 \times 10^{-4}$ seconds^{-1} (Table I), and independent of the initial concentration over a five-fold range (Table II). Since ozone in the gaseous state is known to decompose predominantly as a bimolecular reaction, it was at first thought that its behaviour in solution could be attributed to the presence of impurities acting as catalysts. The reaction in ordinary "laboratory" carbon tetrachloride at 71° C. was almost instantaneous. The "pure" solvent was therefore submitted to various treatments with a view to removing any possible impurity, and various

Table I.—Ozone in Carbon Tetrachloride at 71·0° C.

Time (minutes).	Percentage change.	$k_1 \times 10^4$ (seconds^{-1}).
20	14·0	1·25
40	25·5	1·22
60	36·0	1·24
80	44·5	1·23
100	52·0	1·22
120	58·5	1·22
160	68·0	1·18
200	75·5	1·17

Table II.—Ozone in Carbon Tetrachloride at 71·0° C.

$[O_3]_{\text{initial}} \times 10^4$ (gram-molecule/litre).	Preparation of ozone.	Treatment of solvent.	$k_1 \times 10^4$ (seconds^{-1}).
4·6	Silent discharge	Distilled from P_2O_5	1·16
9·6	Electrolytic from H_2SO_4	Distilled from P_2O_5	1·19
11·3	Silent discharge	Saturated with water	1·17
12·8	Silent discharge	Distilled from P_2O_5; refluxed for several days over mercury.	1·31
20·0	Electrolytic	Distilled from P_2O_5	1·22
21·0	Electrolytic	Distilled from P_2O_5; previously ozonised for 4 hours at the boiling point to remove oxidisable impurities.	1·19

specimens of pure carbon tetrachloride were tried. The ozone itself was also prepared by an alternative method. But no difference was found in the rate of decomposition (Table II), hence it must be concluded that the decomposition of ozone in carbon tetrachloride is unimolecular with respect to the ozone, and that the rate is not determined by impurities in the solvent. Some further data obtained at 54·7° C. are given in Tables III and IV (the concentrations given in Table III were taken from a graph of the actual experimental results.

Table III.—Ozone in Carbon Tetrachloride at 54·7° C.

Time (minutes).	$[O_3] \times 10^4$ (gram-molecules/litre).	$k_1 \times 10^5$ (seconds^{-1}).
0	14·95	
		1·97
100	13·29	
		1·72
200	11·98	
		1·71
300	10·84	
		1·72
400	9·78	
		1·87
500	8·76	
		2·00
600	7·77	
		2·02
700	6·90	
		2·02
800	6·62	
		1·99
900	5·42	
		1·91
1000	4·34	
		Average 1·89

Table IV.—Ozone in Carbon Tetrachloride at 54·7° C.

Initial concentration of ozone $\times 10^3$ gram-molecules per litre.	$k_1 \times 10^5$ (seconds^{-1}).
1·54	1·86
1·50	1·82
1·46	2·39*
1·31	1·77
	Average 1·82

* The results of this experiment gave an excellent titration-time curve. This relatively high value of the constant could, however, not be reproduced, and remains unexplained.

The average values for the unimolecular constants at 54·7° C. and 71·0° C. are $1 \cdot 82 \times 10^{-5}$ and $1 \cdot 23 \times 10^{-4}$ seconds^{-1} respectively; combining these results in the form of the Arrhenius equation, it is found that the kinetics of the decomposition of ozone in carbon tetrachloride solution is given by the relation

$$k_1 = 5 \cdot 82 \times 10^{12} \, . \, e^{-26,160/\mathrm{RT}}.$$

Comparison of the Decomposition of Ozone in the Gaseous State and in Solution.

The gaseous decomposition is bimolecular, the various values found for the energy of activation ranging from Clement's* earlier figure of 26,000 calories to the more recent ones of 27,800 calories given by Belton, Griffith and McKeown,† and 30,900 calories found by Wulf and Tolman.‡ The observed value of the heat of activation for the reaction in solution is thus equal to the lowest recorded value for the gaseous reaction.

Since the order of the reaction differs according to whether we examine it in the gaseous state or in solution, we must, in comparing the rates of decomposition in the two systems, restrict ourselves to a single concentration. In most of the experiments recorded here the concentration of ozone was about $1 \cdot 5 \times 10^{-3}$ gram-molecule per litre; the average times of half-reaction for the dissolved gas are 94 and 635 minutes at 71·0° C. and 54·7° C. From Wulf and Tolman's empirical equation for the bimolecular velocity coefficient of the gaseous reaction

$$k_{\mathrm{bimolecular}} = 2 \cdot 04 \times 10^{17} \, . \, e^{-30,900/\mathrm{RT}} \left(\mathrm{secs.}^{-1} \, . \, \frac{\mathrm{litres}}{\mathrm{gram\text{-}mol.}} \right),$$

inserting the above value for the concentration, we obtain the results given in Table V. Wulf and Tolman worked with ozone-oxygen mixtures and found

Table V.

t° C.	Times of half-completion (minutes), $[\mathrm{O}_3]_{\mathrm{initial}}$ being $1 \cdot 5 \times 10^{-3}$.		$\dfrac{t_{\frac{1}{2}} \text{ gas}}{t_{\frac{1}{2}} \text{ solution}}$.
	For gaseous reaction.	For reaction in CCl_4.	
71·0	2,727	94	29
54·7	26,020	635	41

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* Hinshelwood, 'The Kinetics of Chemical Change in Gaseous Systems' (Oxford, 1929), p. 60; Clement, 'Ann. Physik,' vol. 14, p. 341 (1904).

† Belton, Griffith and McKeown, 'J. Chem. Soc.,' vol. 129, p. 3153 (1926).

‡ Wulf and Tolman, 'J. Amer. Chem. Soc.,' vol. 49, p. 1650 (1927).

k to vary with the pressure of oxygen ; their equation refers to a total pressure of one atmosphere.

Ozone in carbon tetrachloride solution thus disappears 30 to 40 times as rapidly as at a corresponding concentration in the gaseous state (in the presence of oxygen).

It seemed possible that the unimolecular disappearance of ozone in solution was not a simple decomposition but a reaction with the carbon tetrachloride, such as $O_3 + CCl_4 = COCl_2 + Cl_2 + O_2$. If the products of this or of any imaginable reaction between ozone and carbon tetrachloride were extracted with water, the resulting solution would contain chlorine ion. Accordingly, the following experiments were performed. 25 c.c. of a solution, the ozone in which was equivalent to 8·65 c.c. of N/100 sodium thiosulphate, were allowed to react to completion at 71° C. The product was well shaken with dilute baryta, and the extract acidified with nitric acid. 5 c.c. of N/100 silver nitrate were added, which produced an opalescence. Back titration with N/100 ammonium thiocyanate showed that 0·75 c.c. of the N/100 silver nitrate had been used up. A second extraction with alkali of the original solution gave no further chloride. Blank tests on the original carbon tetrachloride and all the other reagents used gave no trace of chloride. These experiments were repeated several times. Thus one must conclude that the solvent is to some extent attacked by the ozone. If the reaction takes place according to the equation given above, each molecule of ozone will yield finally three equivalents of silver nitrate. Thus for every 8·65/2 molecules of ozone decomposing, 0·75/3 appear to react with the solvent, *i.e.*, 1 in 17.

It is evident that oxidation of the solvent does not account for more than a small fraction of the total change. Either, therefore, it is a relatively unimportant side reaction which has nothing to do with the decomposition of the ozone, or it is the first stage of a chain reaction in which about 17 molecules of ozone are decomposed for each initial act. The rate being proportional to $[O_3]$ $[CCl_4]$, and the subsequent stages of the chain being assumed rapid in comparison, the reaction will conform to the unimolecular law. Hypothetical mechanisms for such a chain could easily be invented. Catalysis by chlorine, gradually liberated from the carbon tetrachloride, must be ruled out, since the reaction is not autocatalytic but unimolecular.

If, on the other hand, the reaction between the ozone and the solvent can be regarded simply as a side reaction, we have the very interesting fact that a decomposition, bimolecular in the gaseous state, becomes unimolecular in solution. This would mean that the gaseous reaction was really of the " quasi-unimolecular " type, the molecules being activated by collision but undergoing subsequent spontaneous change. Such reactions, as is well known, appear bimolecular at lower pressures and unimolecular at higher pressures or in the presence of a suitable inert gas. In the present example, the solvent plays the part of the inert gas which communicates the energy of activation. In favour of this interpretation is the fact—not hitherto very well understood—that the bimolecular velocity constant for the decomposition of ozone-oxygen mixtures increases markedly with the total pressure of the system. The value of the heat of activation for the reaction in solution is somewhat lower than the best values for the gaseous reaction ; but if the gas reaction is actually quasi-unimolecular, then the velocity constants found in the " bimolecular " region will not be strictly comparable with one another at different temperatures, and the value of E would not be the true one.

The Decomposition in Carbon Tetrachloride Solution of Ozone Catalysed by Chlorine.

Bodenstein, Padelt and Schumacher,* studying the gaseous reaction at 35° C. and 50° C., where the decomposition of ozone *alone* is slow enough to be ignored, found :—

$$\frac{-d[O_3]}{dt} = k_2\,[Cl_2]^{1/2}\,[O_3]^{3/2}.$$

In the present work we must allow for the no longer negligible rate (k_1) at which the ozone decomposes alone, and thus investigate whether the equation

$$\frac{-d\,[O_3]}{dt} = k_2\,[Cl_2]^{1/2}\,[O_3]^{3/2} + k_1\,[O_3]$$

expresses the results. This gives on integration

$$k_1 t = ln\,\frac{[O_3]_0}{[O_3]_t} - 2ln\left\{\frac{k_2\,[O_3]_0{}^{1/2}\,[Cl_2]^{1/2} + k_1}{k_2\,[O_3]_t\,[Cl_2]^{1/2} + k_1}\right\}.$$

On applying this to the data obtained for three typical runs, we find (Tables VI, VII and VIII) that the value k_2 shows a tendency to rise as the reaction proceeds.

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* Bodenstein, Padelt and Schumacher, ' Z. Phys. Chem.,' B, vol. 5, p. 209 (1929).

Table VI.—Temperature = 54·7° C. $[Cl_2] = 1{\cdot}08 \times 10^{-4}$ gram-molecule per litre.

Time (minutes).	$[O_3] \times 10^3$ (gram-molecule/litre).	$k_2 \times 10^3$ (litre/gram-molecule second^{-1})
0	3·40	—
80	2·55	2·33
120	2·21	2·58
160	1·90	2·56
200	1·64	2·69
240	1·41	2·79
280	1·23	2·94
		Average 2·65

Table VII.—Temperature = 71·0° C. $[Cl_2] = 1{\cdot}48 \times 10^{-3}$ gram-molecule per litre.

Time (minutes).	$[O_3] \times 10^4$ (gram-molecule/litre).	$k_2 \times 10$ (litre/gram-molecule second^{-1}).
0	18·4	—
10	14·2	2·04
20	11·0	2·21
30	8·9	2·04
40	7·7	1·80
60	5·4	1·81
80	3·2	2·30
		Average 2·03

Table VIII.—Temperature = 71·0° C. $[Cl_2] = 1{\cdot}01 \times 10^{-3}$ gram-molecule per litre.

Time (minutes).	$[O_3] \times 10^4$ (gram-molecule/litre).	$k_2 \times 10$ (litre/gram-molecule second^{-1}).
0	15·2	—
20	10·8	1·42
40	7·4	1·67
60	5·0	1·96
80	3·4	2·25
120	2·0	2·06
		Average 1·87

In the following table (IX) are recorded the average values of k_2 found at 54·7° C. and 71·0° C. for solutions containing approximately the same concentration of ozone, but with a 29-fold range of chlorine concentration. $t_{\frac{1}{2}}$

Table IX.

$[O_3] \times 10^3$ (gram-molecule/litre).	$[Cl_2] \times 10^3$ (gram-molecule/litre).	$t_{\frac{1}{2}}$ (minutes).	k_2 (litres/gram-molecule $second^{-1}$).
Temperature = 54·7° C.			
3·08	0·54	259	$2 \cdot 42 \times 10^{-2}$
3·40	1·08	190	2·71
1·46	1·67	207	2·87
3·44	2·68	146	2·39
2·60	5·27	112	2·72
2·88	7·78	83	3·07
2·28	11·03	67	(3·62)
			Average $2 \cdot 70 \times 10^{-2}$
Temperature = 71·0° C.			
2·12	0·206	53	$1 \cdot 7 \times 10^{-1}$
1·10	0·646	44	2·0
1·30	0·776	43	1·7
1·52	1·01	38	1·7
1·84	1·48	28·5	2·0
1·58	1·98	26·5	2·0
1·47	3·20	21	2·4
			Average $1 \cdot 93 \times 10^{-1}$

is the half-life of the ozone, read off from curves obtained by plotting percentage decomposition against time. The values of k_2 are constant within the limits of experimental error for concentrations of chlorine ranging between 5×10^{-4} and 5×10^{-3} gram-molecule per litre; when $[Cl_2]$ exceeds this value there is a definite increase in the value of k_2. By taking the average values of k_2 for the more dilute solutions at both temperatures, we see that

$$k_2 = 2 \cdot 04 \times 10^{16} \, . \, e^{-26,730/RT}.^*$$

We are now in a position to compare the rates of the catalysed reaction in solution and in the gas. Extrapolating our results, it is found that k_2 for the reaction in solution at 50° C. is $1 \cdot 45 \times 10^{-2}$ $seconds^{-1}$. litres per gram-molecule. The mean of 12 experiments carried out by Bodenstein, Padelt and Schumacher (*loc. cit.*) at this temperature for the gaseous reaction is $9 \cdot 50 \times 10^{-3}$. Hence $k_{2\,solution}/k_{2\,gas} = 1 \cdot 53$. The agreement is rather striking, considering the unquestionable complexity of the reaction. The investigation has thus afforded another instance of a chemical reaction—this time a rather unusual one—upon the rate of which the solvent exerts no serious influence.

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* The value given by Bodenstein, Schumacher and Padelt is 20,040 for the gas reaction; but the temperature range over which this was calculated was 35° to 50° C. Since for this complex reaction the Arrhenius equation may not be strictly followed, the two values are perhaps hardly comparable.

The differential equation given by Bodenstein, Padelt and Schumacher contains $[O_3]^{3/2}$ and $[Cl_2]^{1/2}$. Now the variation in the concentration of ozone in carbon tetrachloride solution which is possible practically is somewhat limited. Thus, although our results definitely confirm the proportionality to $[Cl_2]^{1/2}$, it is not possible to say with any degree of certainty whether a somewhat different power of $[O_3]$ would not fit equally well. Assuming, for example, the power to be unity, we have

$$\begin{aligned}\frac{-d\,[O_3]}{dt} &= k_2'\,[Cl_2]^{1/2}\,[O_3] + k_1\,[O_3]\\ &= \{k_2'\,[Cl_2]^{1/2} + k_1\}\,[O_3].\end{aligned}$$

Actually, it is found that this expression holds about as well as the more complicated formula. An example is quoted in Table X below.

Table X.—Temperature = 54·7° C. $[Cl_2] = 1{\cdot}08 \times 10^{-3}$ gram-molecule per litre.

Time (minutes).	$[O_3] \times 10^3$ (gram-molecule/litre).	$\{k_2'[Cl_2]^{\frac{1}{2}}+k_1\} \times 10^5 = k_{obs.} \times 10^5$. (seconds^{-1}).
0	3·40	
		6·06
40	2·94	
		5·93
80	2·55	
		6·06
120	2·21	
		6·20
160	1·90	
		6·13
200	1·64	
		6·22
240	1·41	
		5·85
280	1·23	
		Average 6·06

It now remains to show whether the rate is still strictly proportional to $[Cl_2]^{\frac{1}{2}}$; if this is true then $\{k_{obs.} - k_1\}/[Cl_2]^{\frac{1}{2}}$ should be constant. The extent to which this condition is fulfilled is shown in the following table.

Table XI.—Temperature = 54·7° C. $k_1 = 1{\cdot}82 \times 10^{-5}$ seconds^{-1}.

$k_{\text{obs.}} \times 10^5$ seconds^{-1}.	$[Cl_2] \times 10^3$.	$k_2' \times 10^3 = \frac{(k_{\text{obs.}} - k_1)}{[Cl_2]^{\frac{1}{2}}} \times 10^3$.
4·46	0·54	1·14
6·08	1·08	1·28
5·58	1·67	0·92
7·91	2·68	1·18
10·31	5·72	1·17
13·92	7·78	1·67
17·24	11·03	1·47

Photochemical Measurements.

Bonhoeffer* found that the quantum efficiency of the photosensitised decomposition in the gaseous phase of ozone by chlorine in violet light was 2, and independent of the reactant concentrations. The following experiments were made to determine the quantum efficiency for the same reaction in carbon tetrachloride solution.

As light source a quartz mercury arc was used. An approximately parallel beam of light was produced by a quartz lens, and rendered mono-chromatic by a sheet of Chance's black glass, transmitting only the mercury line 3660 Å. The solutions were contained in quartz cells fitted with ground stoppers and with plane parallel walls 1 cm. apart. The light energy falling on the cell, the amount lost by scattering and reflection at the faces, and the amount transmitted were measured by a quartz spectrograph† fitted with a sodium-quartz photoelectric cell and condenser arranged so that the charging of the condenser, as measured by a Lindemann electrometer, continuously integrated the light received. The instrument had been calibrated directly in quanta received per second by Mr. J. H. Jeffree, using a linear thermopile and a Paschen galvanometer. The cell was first tested for light losses by scattering and reflection.

	Integrated light energy.	Time in seconds.	
Without reaction cell ..	5×10^{-8} quanta per sq. cm.	35·4 35·8 35·2	Average = 35·5 seconds
Cell filled with CCl_4 ..	5×10^{-8} quanta per sq. cm.	37·4 37·0	Average = 37·2 seconds

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* Bonhoeffer, 'Z. Physik,' vol. 13, p. 94 (1923).

† Bowen and Tietz, 'J. Chem. Soc.,' p. 234 (1930).

The fractional light intensity corrected for loss by scattering and reflection from each face of the cell is therefore $\sqrt{(35 \cdot 5/37 \cdot 2)} = 0 \cdot 975$. Two cells, of volume 22 c.c. and area exposed to light 18·0 sq. cm., were filled with solution containing ozone and chlorine ; one was exposed to the light for 2640 seconds, and the other was kept dark. The N/100 sodium thiosulphate titre of the exposed cell was 2·38 c.c. smaller than that for the unexposed cell (the acid titre was 2·30 c.c. smaller). From the average value 2·34, the number of gram-molecules of ozone decomposed in the cell is found to be $11 \cdot 7 \times 10^{-6}$. The ozone and chlorine titres were 7·22 and 6·16 c.c. respectively in the unexposed cell. The corresponding light measurements were as follows :—

	Integrated light energy.	Time in seconds.
Cell with CCl_4 alone ..	5×10^{-8} quanta per sq. cm.	42·0 42·4 } Average = 42·2 seconds
Cell with solution	5×10^{-8} quanta per sq. cm.	46·4 46·4 } average = 46·4 seconds

$$\text{Quanta absorbed} = 5 \times 10^{-8} \times 18 \times 2640 \times \left(\frac{1}{42 \cdot 2} - \frac{1}{46 \cdot 4}\right) \times \frac{1}{0 \cdot 975}$$
$$= 5 \cdot 26 \times 10^{-6}.$$

This gives a quantum efficiency of $11 \cdot 7/5 \cdot 26 = 2 \cdot 22$. The experiment was repeated, $18 \cdot 0 \times 10^{-6}$ gram-molecules being decomposed by $8 \cdot 6 \times 10^{-6}$ quanta : quantum efficiency = 2·09. These results show that the quantum efficiency of the reaction is the same for the dissolved state in carbon tetrachloride as for the gaseous state.

It is remarkable that, whereas the mechanism of the photochemical reaction does not involve long chains, Bodenstein, Padelt and Schumacher conclude from their results on the thermal reaction that chains of the order of 10^4 molecules are set up. Whether this is due to a real difference in mechanism between the photochemical and thermal reactions, or whether the deduction of the thermal chain length is in error through inaccuracy in one or more of the many and varied assumptions which had to be made in calculating it, is hard to decide. The photochemical reaction may conceivably be more complex than it seems. Weigert* found for it a temperature coefficient of 1·17. If this is accurate, it shows that even in the photochemical reaction chains longer than two molecules would be set up at higher temperatures. Further experiments to elucidate these points are now in progress.

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* Weigert, 'Z. Electrochem.,' vol. 14, p. 591 (1908).

Summary.

To compare further reactions in the gaseous state with the corresponding reactions in solution the decomposition of ozone, both alone and sensitised by chlorine, has been investigated using carbon tetrachloride as a solvent.

The catalytic thermal reaction involving chlorine proceeds in solution by a complex mechanism, which appears to be closely similar to that of the gas reaction, and the rate appears to be very nearly the same in both systems.

The photochemical reaction gives a quantum yield of two in solution, again corresponding closely to the gas reaction.

These further examples establish carbon tetrachloride as a "normal" solvent, for purposes of comparison in the case of reactions which cannot be measured in the gas phase.

The uncatalysed thermal decomposition of ozone is unimolecular in solution, and much faster than the bimolecular gas reaction at ordinary pressures. It is possible that the gas reaction is really quasi-unimolecular, and that the solvent allows the limiting velocity to be reached. But an alternative explanation, involving an attack of the solvent by ozone and the setting up of chains, has also to be considered.

We are indebted to Imperial Chemical Industries, Ltd., for a grant by the aid of which apparatus and materials for this investigation have been purchased. One of the authors also desires to express his thanks to the Department of Scientific and Industrial Research for the award of a Senior Research Scholarship.

The Experimental Study of the Rate of Dissociation of Salt Hydrates. *The Reaction* $CuSO_4.5H_2O = CuSO_4.H_2O + 4H_2O$.

By M. L. Smith and B. Topley.

(Communicated by F. G. Donnan, F.R.S.—Received August 7, 1931.)

The work described here forms part of a study of the relationship between absolute reaction velocity and its temperature coefficient in systems of the type $\text{Solid}_1 \rightarrow \text{Solid}_2 + \text{Gaseous Product}$, and of the influence of the gaseous product upon the velocity.

Preliminary Experimental Considerations.

Rate measurements in heterogeneous systems of this kind are subject to certain difficulties which necessitate an extensive examination of the special circumstances of the reaction before much significance can be attributed to the absolute magnitude of an observed rate. It will be convenient to discuss these difficulties in terms of a dissociating salt hydrate,

$$S_1 . nH_2O \rightarrow S_2 . n_2H_2O + (n_1 - n_2)H_2O,$$

in which it is supposed that no solid solution is formed. It is assumed that the course of the reaction is being followed by direct measurement on a spring-balance of the weight change of the solid due to loss of the gaseous product.

The reaction is confined to a zone of molecular thickness which moves through the crystal at a constant linear rate (apart from inhomogeneities in the crystal) and forms the boundary between the two solid phases. Either this linear rate (k) or the proportionate rate of loss of the volatile product per unit area of interface provides an appropriate coefficient of reaction velocity:

$$k = (- dm/dt)(CA)^{-1} . \frac{n_1}{n_1 - n_2} \qquad (1)$$

where $(-dm/dt)$ is the rate of decrease in weight, C is the weight of combined water in unit volume of the reactant solid, and A is the interface area. In general, A at any stage of the reaction depends upon geometrical conditions and upon the relative values of k, and of the probability of spontaneous inception of reaction upon the external surface of the crystal, or the extent to which the latter has been artificially nucleated. These factors determine the form of the reaction curves (percentage reaction : time). Different types of curve found in practice have been discussed previously.*

Sensitivity to Water Vapour and Impedance Effect of the Solid Product.—We have found that the decomposition of several salt hydrates, other than metastable hydrates, is remarkable in that partial pressures of water vapour in the gas phase which are very small fractions of the equilibrium pressures usually have a large effect in depressing the rate of decomposition. The presence of water molecules in the reaction zone affects the measured rate first because the rate is then the difference between the actual rates of the forward and reverse components of the reversible dissociation, and second, because these opposing rates are themselves functions of the concentration of water molecules in the reaction zone; in general, this concentration is governed by an adsorption equilibrium. The relationship between the velocity coefficient and the water vapour partial pressure may therefore be quite complex, and this expectation is borne out by the reactions which we have examined so far; for example, the rate of dehydration of $Mn(C_2O_4)2H_2O$ at first falls sharply with increasing water vapour concentration, then passes through a minimum and rises again to three-fourths of its original value in vacuum, and finally falls again more gradually to zero at the equilibrium pressure. The minimum is reached at a pressure of water vapour about one-thousandth of the vapour pressure of the system. The phenomena are rather simpler with $CuSO_45H_2O$ and with the analogous dissociation of silver carbonate, where there is no minimum.

With the hydrates which we have examined so far ($CuSO_45H_2O$, $Mn(C_2O_4)2H_2O$, $Na(CH_3CO_2)3H_2O$, $BaCl_22H_2O$) this great sensitivity to water vapour is the source of a complication which adds considerably to the difficulty of measuring the true rate (*i.e.*, uninfluenced by water vapour) of the forward reaction. Water molecules eliminated from the crystal lattice by the reaction in the interface diffuse outwards through the layer of S_2 into the vacuum or the gas surrounding the crystal. This outer layer is in an extremely finely divided condition, loosely aggregated to a pseudomorph of the original crystal, but is much more porous to the reaction product than its appearance would suggest. Nevertheless, there is often sufficient resistance to the escape of the water molecules to necessitate applying a correction, especially when considerable thicknesses of S_2 are involved, as in experiments with single crystals. But it must be emphasised that the sensitivity to water vapour is so specific and increases so rapidly as the reaction temperature is lowered that the point has to be examined afresh in every case.

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* Topley and Hume, 'Proc. Roy. Soc.,' A, vol. 120, p. 211 (1928).

If the water vapour is absorbed or frozen out with liquid air, the number per unit area of product water molecules (adsorbed but not combined) in the reaction zone adjusts itself to a stationary value which is a function of the total impedance experienced by the water molecules between the reaction zone and the part of the reaction vessel in which they are finally absorbed, and of the reaction velocity coefficient and its sensitivity to water vapour. When the experiment is done at very low pressures the impedance is simply that due to the outer layer of S_2, and increases with its thickness.

In principle, therefore, by calculating values of k from equation (1) at various stages through the reaction and extrapolating back to zero thickness of S_2 the impedance effect is eliminated. In practice for any particular reaction this can only be done successfully over a certain range of velocity which must be found by experiment for the size of crystal imposed by other considerations.

Calculation of the Temperature of the Solid during Reaction.—During the decomposition the temperature of the solid is below that of its surroundings. Within a few minutes of the start of the reaction a stationary state with respect to temperature is reached, in which heat interchange with the surroundings balances the rate at which energy is consumed by the endothermic dissociation process. Decomposition in a vacuum is the most important case in practice. With a suitable arrangement of apparatus the crystal can be regarded as hanging in a complete enclosure with walls at a known absolute temperature. The radiational interchange then establishes a stationary state expressed by

$$\lambda \, . \, \frac{-dm}{dt} = \mathrm{S} 2\pi \int_0^\infty \{f(\nu, \mathrm{T}) - f(\nu, \mathrm{T}')\} \alpha_\nu \, d\nu, \tag{2}$$

where

λ = heat of reaction in calories per gram H_2O.

$\frac{-dm}{dt}$ = rate of decomposition in grams per second.

S = external area of the crystal.

$f(\nu, \mathrm{T})$ and $f(\nu, \mathrm{T}')$ = Planck radiation function for the temperature of the thermostat and of the crystal.

α_ν = absorption coefficient of the crystal, approximately the same at T and T′.

When the assumption that the solid behaves as a perfectly absorbing body can be justified for the frequency range which is of importance in the radiation function at T and T′, the expression reduces to

$$\lambda \, . \, \frac{-dm}{dt} = \mathrm{S} \, . \, 1{\cdot}38 \times 10^{-12} \{\mathrm{T}^4 - \mathrm{T}'^4\}. \tag{3}$$

Under the experimental conditions* the degree of self-cooling is governed primarily by the reaction rate, since heats of dissociation do not differ in order of magnitude, and the area factor S cannot be arbitrarily altered independently of $-dm/dt$. But the region of absolute temperature in which the reaction is being studied is also of importance since approximately $(\mathrm{T} - \mathrm{T}')$ varies as $1/\mathrm{T}^3$.

When the reactant solid is suspended in an atmosphere of an inert gas (hydrogen) at a few millimetres pressure the thermal conductivity so far reduces the self-cooling that for some purposes it is no longer serious, and the residual effect can be roughly calculated. But the presence of the gas causes some obstruction to the free escape of the water molecules.

Limitations to the Range of Measurements.—It will be clear from what has been said that with hydrates, which are very sensitive to water vapour, we find ourselves to some extent in this dilemma: that with measurements in the region of relatively high rates a correction is required on account of the self-cooling, which may easily amount to 10° or 20°, and this must be calculated from data for the infra-red absorption of the solid which are not easily obtained; on the other hand, if this difficulty is avoided or greatly lessened by the use of an inert gas, then a further correction may be necessary on account of the impedance to the diffusion of the water vapour away from the vicinity of the crystal. In the region of the slowest rates measurable in practice the self-cooling is negligible, but we encounter another difficulty, namely, that although the rate of the reaction producing the water molecules, and with it the number of free water molecules per unit area of the reaction zone under stationary state conditions, is exponentially decreased by lowering the temperature of reaction, yet the sensitivity to water vapour may be increased to an extent which outweighs this. Hence there may be both an upper and a lower limit to the temperature range over which the true rate of dissociation, uninfluenced by the recombination reaction, can be measured, and these limits have to be decided by a consideration of the behaviour of the reaction itself. In the case of the dehydration of $CuSO_45H_2O$ to the monohydrate we find the limits to be about 0° to 45°.

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* The temperature difference between the external surface of the partly dehydrated crystal and the interface can be shown to be negligible, even assuming a very low value for the thermal conductivity of the solid product.

These unavoidable difficulties are more troublesome in connection with the question of the functional dependence of rate upon temperature, where a wide range is particularly desirable, than for an enquiry into the general nature of the reaction, for which the most favourable temperature may reasonably be chosen.

The Reaction $CuSO_45H_2O \longrightarrow CuSO_4H_2O + 4H_2O$.

During the progress of this work two other investigations of the same reaction have been completed by other workers. Garner and Tanner* measured the rates of dehydration in very high vacuum, at a series of temperatures, of comparatively large single crystals of the pentahydrate. Part of our own work overlaps with that of Garner and Tanner, but covers a wider range of conditions; we draw a different conclusion from the results. But we wish here to record the assistance given to us by their work, which enabled us to simplify our own procedure; and the numerical agreement of the results so far as they cover the same ground, was encouraging. The other investigation is one now in course of publication by Hume and Colvin, who have very kindly communicated their results to us in advance. This work, although done with a different object in view, will have an important bearing upon our work. The reproducibility of the rates with different preparations of the pentahydrate gives us confidence that the reaction chosen is a suitable one for our present purpose. References to earlier work are given by Hume and Colvin.

Apparatus and Experimental Method.

The apparatus was evolved to meet the conditions imposed by the sensitivity to water vapour. The experiments are of two kinds: "static," done in a vacuum or in an atmosphere of stationary gas of fixed composition and pressure; "flow," done in a stream of hydrogen or other gas of which the composition, pressure and rate of flow are controlled. The arrangement is shown diagrammatically in fig. 1. The silica spring-balance (sensitivity 1·662 mgm. per millimetre), cathetometer and mounting, and the counterpoise arrangement for raising the thermostats round the reaction vessel, have already been described.†

It was found by calculation from the temperature coefficient of elasticity of fused silica, and verified by measurement, that the extension of a spring of this sensitivity decreases by 0·0225 mm. per 1° rise in temperature. It is therefore necessary to keep the temperature of the spring-balance case constant to within 0·1°. This is done by an air thermostat without mechanical stirring.

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* 'J. Chem. Soc.,' vol. 132, p. 47 (1930).

† Spencer and Topley, 'J. Chem. Soc.,' vol. 131, p. 2633 (1929).

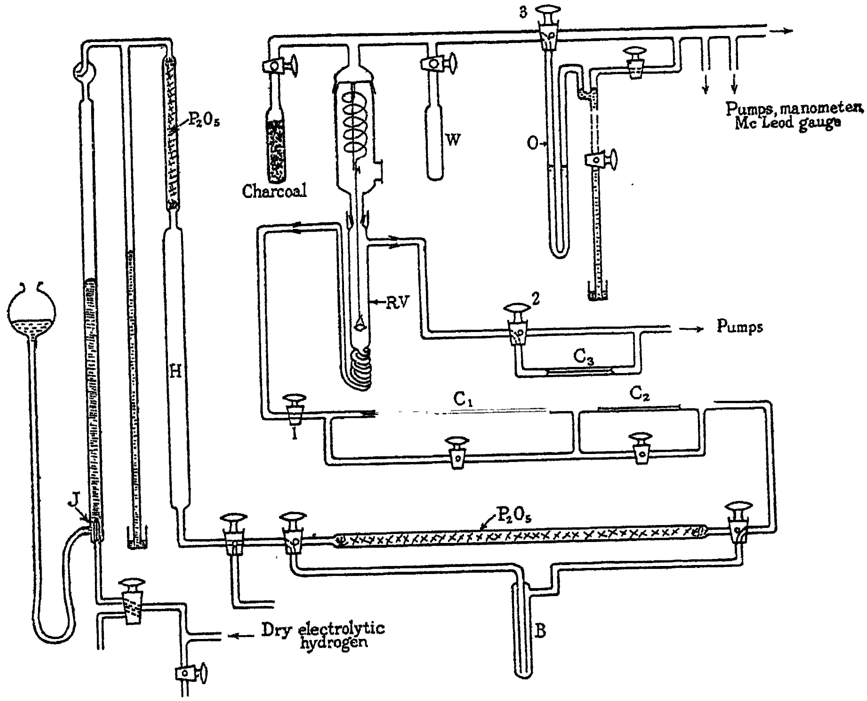

Fig. 1.

The thermostat (not shown in the diagram) consists of a wooden box thickly covered with felt, with narrow glass windows. The heating wire was wound on the inside of the lower part of the walls, and caused a convection current to move round inside the box and through a small opening in the top. The regulator was constructed with two long toluene-filled arms running one up each side of the glass spring-balance case, practically touching it. The temperature difference was 0·4° for the 50 cm. height of the air thermostat and at any one place the fluctuation was less than 0·1°.

The reaction vessel consists of the tube RV, 30 cm. long and 2·3 cm. internal diameter, detachable by the wide joint from the spring-balance case and by the two narrow joints from the inflow and outflow tubes. The crystal is suspended in a fine wire stirrup, or on a thin glass pan, by means of a long quartz fibre reaching to within a few centimetres of the spiral tube at the bottom of RV. This reaction vessel is surrounded by a deep Dewar vessel containing a regulator and heating coil, and filled either with water or oil stirred by an air current or by ground ice. The " outflow " tube is connected through the tap (2) either directly to the Hyvac and diffusion pumps, or indirectly through a short length of wide capillary tube. The reaction vessel is also in direct communication through the spring-balance case with a charcoal-liquid-air bulb and a bulb containing glass wool moistened with water (W). The oil manometer (O) contains " Apiezon " oil, stated to have a vapour pressure less than 10^{-7} mm. Differences of level can be read with a cathetometer to an accuracy corresponding to 0·003 mm. of mercury. The right-hand limb is evacuated and guarded by a mercury seal. The left-hand limb leads through the tap (3) either to the apparatus or to the pumps. This tap also permits the oil manometer to be shut off completely and the apparatus to be connected straight through to the pumps and to a mercury manometer and a McLeod gauge.

" *Static* " *Experiments.*—The tap (1) is closed. In experiments in which it is desired to remove the water vapour as rapidly as possible, a layer of fresh phosphorus pentoxide is placed at the bottom of the reaction vessel, and a high vacuum maintained by the pumps and by the charcoal-liquid-air bulb. For experiments of long duration (measurements at 0° required as much as 100 hours) the ground joints were sealed with Picein wax and the vacuum maintained overnight by the charcoal-liquid-air bulb alone.

Other " static " experiments were done in the presence of known pressures of hydrogen or other gas, either to provide a means of heat conduction to the crystal, or to study the specific effect of gases such as sulphur dioxide or ammonia upon the interface reaction. Constant water vapour pressures were maintained by adjusting the temperature of the bulb (W) by acetone plus solid carbon dioxide mixtures; the rate of production of water vapour by the crystal was not so great that the impedance of the tubes leading to this bulb became important. Naturally this method was available only in the complete absence of any other gas. Higher water vapour pressures were measured on the oil manometer.

" *Flow* " *Experiments.*—In some cases there are disadvantages attaching to the static method. Thus the use of phosphorus pentoxide in the reaction vessel is unsatisfactory at temperatures above about 40° except for short periods, since the freshly distilled active form distils on to the reacting solid to a detectable extent during a long experiment in vacuum. When " static " experiments are done in the presence of hydrogen the water vapour produced by the reaction diffuses through one or two centimetres of the gas down to the phosphorus pentoxide, and a gradient of water vapour concentration is set up resulting in a partial pressure in contact with the crystal which cannot be estimated at all accurately. It is a matter for experiment to decide whether in any particular case the poisoning effect of this water vapour is serious enough to invalidate static experiments with hydrogen present; with $CuSO_4 5H_2O$ useful information is obtained at 20° and above, but not at 0°, while with $Mn(C_2O_4)2H_2O$ the static method is almost useless.

The "flow" method designed to avoid these difficulties has proved very satisfactory. When it is desired simply to remove the self-cooling, hydrogen is the appropriate gas on account of its high conductivity and slight tendency to adsorb. When it is desired to study the effect of another gas, *e.g.*, water vapour, it is an easy matter to add known proportions to the hydrogen stream, by saturating the hydrogen in the bubbler B.

The flow method, however, always results in a certain partial pressure of water vapour round the crystal. The region in which this has proved to be of most interest is from 0·001 mm. to 0·3 mm.; at higher pressures the static method is always available. The flow method allows partial pressures to be obtained over the whole of this range. The hydrogen flows in a turbulent stream up the reaction tube at linear speeds of the order of 1000 cm. a minute, and pressures of from 1 to 5 mm. The water vapour leaving the crystal surface is caught in this stream, and we may assume that complete mixing takes place in the immediate neighbourhood of the crystal surface, as a rough calculation taking account of the enormous rate of diffusion through the low pressure of hydrogen shows; the layer of gas containing the concentration gradient is very thin, and the excess concentration at the surface over the concentration in the gas stream is negligible.

Then we have

$$p_{H_2O} = \frac{m_1 + m_2}{M + m_1 + m_2} \cdot (P), \qquad (4)$$

where

p_{H_2O} = partial pressure of water vapour in the gas surrounding the crystal.

(P) = total pressure in the reaction tube, registered by the oil manometer.

m_1 = number of gram molecules of water liberated by the reaction in unit time.

m_2 = number of gram molecules of water entering the reaction vesse in the gas stream in unit time.

M = number of gram molecules of hydrogen entering the reaction vessel in unit time.

The diagram shows how the hydrogen stream was obtained, and it is only necessary to refer to certain details. Since it was desired to vary the flow rate and the flow pressure independently, the exit tube from the reaction vessel was alternatively connected to the Hyvac pump through a short length of 4 mm.-bore tubing (to steady the flow) or through a short length of capillary tube (c_3). The flow rate was governed by the system of capillary tubes (c_1) and (c_2) or (c_1 c_2), and by adjusting the hydrogen pressure in the reservoir H. This is automatically maintained constant at any desired pressure between 700 and 70 mm. by the mercury bubbler shown; the capillary jet (j) is 4 cm. long and 0·02 cm. bore, and the diameter of the mercury column 3 cm. A further sensitive control upon flow rate and flow pressure was obtained by heating c_1, c_2 and c_3 (bore = 0·02 cm.) which were wound with nichrome wire and lagged.

Tests with a thermometer showed that the gas reaches the thermostat temperature by the time it has passed through the spiral tube at the bottom of RV. No difficulty is introduced by the uplift exerted by the gas stream upon the hanging crystal, which, although considerable (up to 1 mm.), remains perfectly constant. An earlier form of the apparatus, in which the warm gas flowed over the silica spring as well, failed because the temperature of the latter could not then be kept steady.

Experiments done in Vacuum.

Most of the experiments have been done with single crystals, which has the advantage over a sample consisting of a large number of small crystals on the glass pan that the interface area and the radiation equilibrium can be calculated more closely. Starting with crystals which have not been artificially "nucleated," the usual sigmoid reaction curve is obtained, the maximum rate with crystals weighing about 50 mgms. being at about 15 per cent. decomposition. Hume and Colvin discuss the form of this curve; our experience accords with theirs and there is no need to refer further to the matter here.

Garner and Tanner (*loc. cit.*) found that at 56° (but not at 46° or below) the tri-hydrate is formed instead of the mono-hydrate; the curve of weight loss against time showed a sharp bend at about the composition of the tri-hydrate, and inspection of the product showed that the whole of the original penta-hydrate had reacted. The formation of the tri-hydrate at the higher temperature is a very interesting point, and is referred to again later. We have found no evidence that the tri-hydrate is formed between 0° and 50°, the highest temperature at which we have made careful measurements. Thus at 50° in a vacuum the rate at different stages of the decomposition is :—

Fraction decomposed	0·1	0·2	0·3	0·4	0·5	0·6	0·7
Rate (mgm./min. cm.^{2})	0·192	0·162	0·134	0·128	0·110	0·104	0·089

The " fraction decomposed " refers to a final loss of $4H_2O$, and the rates are not corrected for the decrease in the interface area. The dehydration is evidently a perfectly continuous process at this temperature.

Following the procedure of Garner and Tanner, the accelerating stage at the beginning of the reaction can be reduced to 1 or 2 per cent. by rubbing the crystal surface beforehand with the mono-hydrate powder. Garner and Tanner also found that the linear rate of propagation does not differ by as much as 10 per cent. along different crystal axes; Hume and Colvin assume equality. As a first approximation we shall make the same assumption.

Elimination of the Impedance Effect due to the Lower Hydrate.—After the first few per cent., as the reaction proceeds the rate decreases (*a*) because the interface area decreases, (*b*) because the impedance effect due to the solid product increases, and (*c*) through a secondary effect, since the decreased rate involves less self cooling, so that the rate falls less rapidly than it otherwise would.* Calculation shows that the stationary state defined by equation (3), after it has once been established, may be assumed to adjust itself continuously to the changing reaction rate.

The method we have used to eliminate these changing factors is to plot the observed rates of change of weight at 10, 20, 30, 40 and 50 per cent. decomposition, and to extrapolate the curves back to 0 per cent. The intercept on the axis of rate gives the true rate of decomposition, *i.e.*, the rate which the crystal would exhibit if the interface were fully developed with a negligible thickness of the mono-hydrate. The area of this interface is the superficial area of the original crystal and the reaction temperature is the " stationary state " temperature corresponding to and calculable from the extrapolated rate. The dimensions of the pseudomorph obtained at the end of the reaction are measured with a travelling microscope, and the calculated area substituted for A in equation (1) and for S in equation (3).

Four typical experiments covering the temperature range will show what is involved in this extrapolation, in practice, in this reaction. In Table I, for

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* This secondary effect may even cause the rate *per unit area of interface* to increase; in fact, this would appear to be cause of the increase observed by Garner and Tanner at the higher temperatures.

Table I.

Thermostat temperature 43·15° (vacuum).

Fraction decomposed (α).	0.	0·1.	0·2.	0·3.	0·4.	0·5.
Observed rate, mgm. min.$^{-1}$	0·0960	0·0823	0·0727	0·0653	0·0586	0·0524
Interface area, cm.^{2}	0·788	0·731	0·677	0·621	0·567	0·503
Rate per cm.^{2}	0·122	0·113	0·108	0·106	0·104	0·104
Impedance	1·00	0·93	0·88	0·87	0·85	0·85
Degrees self-cooling	8·43	7·37	6·66	6·10	5·55	5·03

Thermostat temperature 22·25° (vacuum).

Fraction decomposed (α).	0.	0·1.	0·2.	0·3.	0·4.	0·5.
Observed rate, mgm. min.$^{-1}$	0·0213	0·0164	0·0139	0·0124	0·0110	0·00985
Interface area, cm.^{2}	0·552	0·513	0·475	0·436	0·398	0·354
Rate per cm.^{2}	0·0387	0·0320	0·0292	0·0284	0·0276	0·0278
Impedance	1·00	0·83	0·75	0·73	0·71	0·72
Degrees self-cooling	3·13	2·47	2·13	1·93	1·73	1·61

Thermostat temperature 0° (vacuum).

Fraction decomposed (α).	0.	0·1.	0·2.	0·3.	0·4.	0·5.
Observed rate, mgm. min.$^{-1}$	0·00260	0·00228	0·00196	0·00165	0·00133	0·00102
Interface area, cm.^{2}	0·759	0·705	0·651	0·598	0·543	0·485
Rate per cm.^{2}	0·00343	0·00323	0·00301	0·00276	0·00244	0·00211
Impedance	1·00	0·94	0·88	0·80	0·71	0·62
Degrees self-cooling	0·35	0·31	0·27	0·24	0·20	0·17

Thermostat temperature 22·25°. $p_{H_2} = 0·46$ mm. Hg.

Fraction decomposed = α.	Observed rate mgm. min.$^{-1}$.	Fraction decomposed = α.	Observed rate mgm. min.$^{-1}$.
0·022	0·0268	0·242	0·0176
0·035	0·0243	0·258	0·0170
0·049	0·0233	0·275	0·0160
0·066	0·0241	0·300	0·0151
0·082	0·0228	0·321	0·0146
0·098	0·0209	0·350	0·0146
0·114	0·0207	0·378	0·0138
0·134	0·0203	0·398	0·0133
0·155	0·0191	0·418	0·0128
0·189	0·0191	0·437	0·0125
0·226	0·0178		

the experiments in vacuum the first row of the data for each temperature gives the actual rates observed, in milligrams per minute, the value at α = 0 being obtained by extrapolating the curve by hand. The interfacial areas at different stages are calculated from the linear dimensions of the crystal by assuming that the reaction is propagated inwards uniformly. The rates per square centimetre are the quotients of corresponding figures in the first two rows. The variation of these with α is an empirical measure of the combined effect of the impedance, the decrease in the extent of self-cooling, and any error involved in the method of calculating the areas. The relative values of the rates per square centimetre through the reaction (taken as an indication simply of the impedance effect, since this is the main influence) are given in the fourth row, and the extent of the self-cooling in the last row. The rates after 50 per cent. decomposition do not influence the extrapolation over the first 10 per cent., and so are not of interest in this connection. The corrected rates are derived only from the first row of data and the external area of the crystal; the other figures are added for later reference.

The last set of data refer to an experiment done by the "static" method with hydrogen present; they are of interest in that measurements were obtained nearer the beginning of the reaction than usual. The left-hand column gives the mean amount of decomposition at the stage at which the differential rates in the other column were measured over short intervals of time.

The Self-cooling of $CuSO_4 5H_2O$ *Crystals in a Vacuum.*

The finely divided condition of the mono-hydrate layer ensures that the partially decomposed crystal will be opaque, because of the multiple reflections of incident radiation penetrating into the surface layers; moreover, the water of crystallisation and the sulphate ion in a crystal of the thickness used would transmit little radiation of the wave-lengths important at the temperature considered.

The possibility of *reflection* is more serious. In the Planck function the maximum density of radiation in the thermostated reaction vessel lies between 9 and 10 μ at 0° to 43° C. The sulphate ion possesses selective reflectivity in this region; since the outer surface of the pseudomorph is smooth enough to reflect visible light slightly, it was a possibility that infra-red radiation would be strongly reflected. This uncertainty was removed by direct measurements of the reflection of radiation of the important wave-lengths from the surface of a large crystal partially dehydrated in vacuum. The measurements were done for us by Mr. A. B. D. Cassie, who very kindly wrote the following note on this point.

"Radiation from a Nernst filament passed through a Hilger D42 spectrometer with a rock-salt prism and slit width of 0·02 inches, *i.e.*, slit widths containing a frequency range of 20 cm.$^{-1}$. The radiation diverged from the telescope slit to a concave mirror which gave an image of the slit, approximately three-fourths its original size, on either a plane surface of the dehydrated crystal or on the silvered surface of a plane mirror. Radiation diverged from this image to a second concave mirror, which converged it on the thermopile elements. The surface of the dehydrated crystal fortunately reflected sufficient red light to give a visible image of the telescope slit at the thermopile."

"The procedure was therefore as follows: the crystal was first placed in position so that the image of the telescope slit fell on the thermopile. The wave-length drum was rotated to 7 μ, and between 7 and 10 μ galvanometer deflections were noted on opening a shutter between the Nernst filament and the collimator slit. Only between approximately 8·7 μ and 9·6 μ did the galvanometer give appreciable deflections. These reached a maximum of 3·5 cm. near 9·3 μ. The crystal was now replaced by the plane silvered mirror. This mirror was adjusted to give an image of the telescope slit on the thermopile. The drum was set at 9·3 μ, and on opening the shutter the galvanometer spot was deflected through approximately 150 cm. Hence the energy reflected by a dehydrated copper sulphate crystal in this region has a maximum of approximately 2 per cent. near 9·3 μ."

We conclude, therefore, that for our purposes the crystals may be treated as full radiators, and the self-cooling calculated by equation (3).

An accurate estimate of the increase in heat content of the dissociating system is available from the data of Carpenter and Jette for the dissociation pressures* of the two systems $CuSO_4 3H_2O \rightleftarrows CuSO_4 H_2O + 2H_2O$ and $CuSO_4 5H_2O \rightleftarrows CuSO_4 3H_2O + 2H_2O$. Since the decomposition takes place into a vacuum, we take

$$\Delta H = 2RT^2 \left. \frac{d\ln p_{5\rightarrow 3}}{dT} + \frac{d\ln p_{3\rightarrow 1}}{dT} \right] - 4RT,$$

which gives 702·3 cal. absorbed per gram H_2O lost, at the mean temperature of 33° C., and we take this value for λ in equation (3).

Absolute Rates of the Reaction $CuSO_4 5H_2O = CuSO_4 H_2O + 4H_2O$ *at different Temperatures.*

Table II contains the summarised results of experiments in vacuum with phosphorus pentoxide present in the reaction vessel. The rates in the third column have been corrected for the impedance effect by the extrapolation method, and have been reduced to milligrams per square centimetre per minute. The self-cooling correction has been calculated from the mean rate per unit area at each temperature.

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* Carpenter and Jette, 'J. Amer. Chem. Soc.,' vol. 45, p. 583 (1923).

Table II.

Column 1 = weight of original crystal in milligrams.
„ 2 = external area of crystal in square centimetres.
„ 3 = rate corrected to $\alpha = 0$ in milligrams per square centimetre per minute.
„ 4 = mean rate.
„ 5 = absolute temperature of thermostat.
„ 6 = number of degrees of self-cooling.
„ 7 = corrected temperature of crystal.

1.	2.	3.	4.	5.	6.	7.
56·0 69·2 64·0 42·4 65·7	0·648 0·765 0·740 0·579 0·759	0·00332 0·00283 0·00330 0·00282 0·00343	0·00323	273·0	0·3	272·7
69·2	0·765	0·00562	0·00562	278·0	0·6	277·4
69·2	0·765	0·00868	0·00868	282·95	0·85	282·1
65·7 69·2	0·759 0·765	0·0276 0·0250	0·0263	293·0	2·2	290·8
47·0 62·4 42·4	0·552 0·797 0·579	0·0383 0·0292 0·0387	0·0354	295·25	3·0	292·25
56·4	0·631	0·0459	0·0459	298·0	3·5	294·5
64·0 56·0	0·740 0·648	0·0712 0·0843	0·0778	308·02	5·79	302·23
55·2 66·0	0·648 0·122	0·112 0·122	0·117	316·15	8·14	308·01

In fig. 2 the reciprocals of both sets of absolute temperatures are plotted against the logarithms of the rates. It will be noticed that the reciprocal *thermostat* temperatures lie upon a pronounced curve, but the corrected temperatures are in agreement with the heavy straight line, which takes account also of other points obtained from experiments done in the presence of hydrogen.

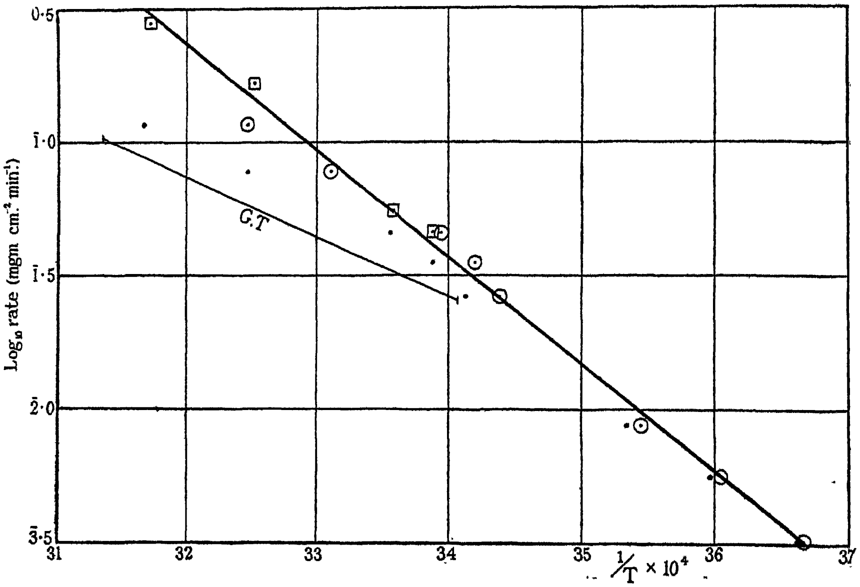

FIG. 2.—⊡ Rates in presence of Hydrogen; • Rates in vacuum (uncorrected); ⊙ Rates in vacuum (corrected); G.T., Garner and Tanner mean line.

Rate Measurements in the Presence of Hydrogen.

The greater part of the self-cooling can be prevented by a small pressure of hydrogen in the reaction vessel. Since the thermal conductivity rises to a constant value with increasing pressure (the actual pressure at which the maximum conductivity is reached naturally depends upon the dimensions of the crystal and the reaction vessel; in the present case the maximum is apparently reached with less than 0·2 mm.), whereas the diffusion coefficient of water vapour through the gas decreases continuously, it was anticipated that the reaction rate would at first rise, and subsequently fall. This result was found at the higher temperatures (43° to 22°), but at 0° the sensitivity to water vapour is so great and the self-cooling so slight that only the decrease was observed.

Table III records the thermostat temperatures, hydrogen pressures in millimetres of mercury, and the rates in milligram H_2O lost per square centimetre per minute. The rates at $p_{H_2} = 0$ are " vacuum " rates taken from Table II. The individual results at 43·15° and at 22·25° were all obtained from separate experiments with different single crystals, the rates being extrapolated back to $\alpha = 0$ as already described. The results at 35·02° and at 0° were obtained by altering the hydrogen pressure in a single experiment, at each temperature;

Table III.

Temperature 43·15°.		Temperature 35·02°.		Temperature 35·02°.	
p_{H_2} (mm.).	Rate.	p_{H_2} (mm.).	Rate.	p_{H_2} (mm.).	Rate.
0	0·117	0	0·0778	0	0·0778
0·040	0·163	0·11	0·176	0·2	0·148
0·089	0·237	0·17	0·183		
0·130	0·239	0·32	0·184		
0·190	0·280	0·58	0·189		
0·235	0·272	0·83	0·183		
0·480	0·270	1·13	0·179		
1·030	0·255	3·63	0·157		

Temperature 25·0°.		Temperature 22·25°.		Temperature 0°.	
p_{H_2} (mm.).	Rate.	p_{H_2} (mm.).	Rate.	p_{H_2} (mm.).	Rate.
0	0·0459	0	0·0354	0	0·00323
0·2	0·0552	0·03	0·0454	0·029	0·00257
		0·09	0·0425	0·039	0·00251
		0·13	0·0475	0·106	0·00207
		0·14	0·0419		
		0·29	0·0462		
		0·46	0·0420		
		0·77	0·0502		
		2·09	0·0433		

in this case the correction to $\alpha = 0$ had to be made by comparison with other experiments. There are also two results obtained in an experiment in which one hydrogen pressure only was employed at 25·0° and at 35·02°.

By plotting these results the following values were obtained for the maximum rates, uninfluenced by water vapour, in the presence of hydrogen :—

Table IV.

Thermostat temperature.	Rate.	Self-cooling.	Corrected temperature.
° 43·15	0·280	0·9	315·3 Abs.
35·02	0·185 0·148		
	Mean 0·167	0·54	307·5
25·0	0·0552	0·18	297·8
22·25	0·0460	0·15	295·1

The much smaller amount of self-cooling that still remains in the presence of hydrogen is calculated on the assumption that the full thermal conductivity of the gas is reached when the rate is a maximum, making allowance for the combined effect of gas conductivity and radiation. These points are included in fig. 2.

The Influence of Water Vapour.

Preliminary experiments showed that the sensitivity to water vapour (expressed as the relative lowering of rate by a given small pressure of water vapour) is several hundred times greater at 0° than at 60°. The effect was examined more closely at intermediate temperatures.

In "static" experiments the required pressure was established in the reaction vessel by evacuating very thoroughly and then opening the tap to the bulb containing glass wool and water; the latter was regulated to within 0·1° of the required temperature by stirring in solid carbon dioxide into an acetone bath surrounding the bulb. Pressure equilibrium between the reaction vessel and the bulb appeared to be established sufficiently rapidly through the connecting tube (1·3 cm. diameter); at any rate the rate of decomposition responded immediately to a decrease in the temperature of the bulb, and became constant as soon as the latter, so that the bulb appears to take up the water vapour produced quite efficiently. It was not considered advisable to attempt to maintain constant pressures lower than 0·004 mm.

Measurements were made at 22·25° with two different crystals, each at a series of pressures. In order to be able to eliminate the effect of changing interface area and impedance by the extrapolation method, rate measurements for each pressure were made at different stages of the reaction, so that a curve connecting rate and fraction decomposed is obtained appropriate to each pressure. The importance of this lies in the fact that (as discussed in a later paragraph) the impedance effect decreases markedly as the water vapour pressure increases.

In Table V the figures in the third column are the rates obtained by extrapolation. Corresponding to the different rates there must be different amounts of self-cooling of the crystals; this has been taken account of as follows. The cooling has been calculated assuming heat transfer by radiation only, and ignoring the conductance of the small pressures of water vapour. The rates have then been corrected up to 22·25° again by the temperature coefficient which applies in vacuum; where the error in this procedure is likely to be large, the correction itself is very small. The corrected rates are given in the last column.

Table V.

Temperature 22·25°.

Experiment number.	p_{H_2O} (mm. Hg).	Rate (mgm./cm.^{2} min.).	Self-cooling.	Rate correction.
(Mean)	(Vacuum)	0·0354	3·0	0·0420
25	$0{\cdot}44 . 10^{-2}$	0·0206	1·8	0·0240
33	$0{\cdot}46 . 10^{-2}$	0·0207	1·8	0·0241
25	$0{\cdot}90 . 10^{-2}$	0·0170	1·5	0·0193
25	$1{\cdot}50 . 10^{-2}$	0·0140	1·3	0·0156
25	$2{\cdot}20 . 10^{-2}$	0·00965	0·93	0·0104
33	$3{\cdot}17 . 10^{-2}$	0·00505	0·50	0·00527
33	$4{\cdot}02 . 10^{-2}$	0·00236	0·26	0·00241
25	$4{\cdot}50 . 10^{-2}$	0·00223	0·25	0·00228

Experiments on the influence of water vapour have also been done by the "flow" method.

Table VI.

Temperature 25·0°.

Flow rate c.c./min.	p_{H_2} (mm.).	Rate.	p_{H_2O} (mm.) from reaction.	p_{H_2O} (mm.) added.	p_{H_2O} (mm.) total.
17·8	2·45	0·0383	$0{\cdot}427 . 10^{-2}$	—	$0{\cdot}427 . 10^{-2}$
17·8	6·53	0·0325	$0{\cdot}885 . 10^{-2}$	—	$0{\cdot}885 . 10^{-2}$
17·8	2·40	0·0229	$0{\cdot}206 . 10^{-2}$	$1{\cdot}623 . 10^{-2}$	$1{\cdot}829 . 10^{-2}$
17·8	6·50	0·0041	$0{\cdot}104 . 10^{-2}$	$4{\cdot}391 . 10^{-2}$	$4{\cdot}495 . 10^{-2}$

Temperature 35·02°.

17·5	2·37	0·0890	$0{\cdot}681 . 10^{-2}$	—	$0{\cdot}681 . 10^{-2}$
17·5	6·50	0·0780	$0{\cdot}792 . 10^{-2}$	—	$1{\cdot}792 . 10^{-2}$
17·5	2·33	0·0733	$0{\cdot}460 . 10^{-2}$	$1{\cdot}592 . 10^{-2}$	$2{\cdot}052 . 10^{-2}$
17·5	6·50	0·0497	$0{\cdot}969 . 10^{-2}$	$4{\cdot}438 . 10^{-2}$	$5{\cdot}405 . 10^{-2}$

The first column records the number of cubic centimetres of hydrogen (reduced to N.T.P.) streaming through the reaction vessel per minute; the hydrogen pressure (millimetres of mercury) in the reaction vessel is given in the second column. The third column gives the reaction rate corrected for the impedance effect. The fourth column gives the partial pressure of water vapour arising from the dehydration process itself. The last two columns give the partial pressure added to the hydrogen stream before it enters the reaction vessel, and the total partial pressure.

The changing sensitivity to the presence of water vapour is best seen by comparing the rates at some arbitrary partial pressure with the rates in vacuum at the same temperatures :—

Temperature	35·02°	25·0°	22·25°
Ratio of rate at $p_{H_2O} = 0 \cdot 04$ mm. to rate in vacuum	0·35	0·12	0·06

Qualitatively we have found also that the rate at 60° is only reduced to roughly one-tenth by 11·28 mm. of water vapour.

To a large extent the impedance effect of the mono-hydrate layer disappears when the dehydration takes place in the presence of water vapour. Thus, at 22·25°, the "impedance" calculated as in connection with the experiments in vacuum is much nearer to unity than the corresponding values in Table I.

Table VII.

Temperature 22·25°.

Fraction decomposed = α	0·1.	0·3.	0·4.	0·5.
p_{H_2O} =	$0 \cdot 46 . 10^{-2}$ mm.			
Impedance	0·83	0·60	—	0·52
p_{H_2O} =	$0 \cdot 90 . 10^{-2}$ mm.			
Impedance	0·96	0·84	—	0·90
p_{H_2O} =	$1 \cdot 50 . 10^{-2}$ mm.			
Impedance	0·96	1·01	0·92	—
p_{H_2O} =	$2 \cdot 20 . 10^{-2}$ mm.			
Impedance	1·00	1·01	1·02	—
p_{H_2O} =	$3 \cdot 17 . 10^{-2}$ mm.			
Impedance	0·98	0·91	—	0·83
p_{H_2O} =	$4 \cdot 02 . 10^{-2}$ mm.			
Impedance	1·00	1·00	—	1·04

With the exception of the irregularity with $3 \cdot 17 . 10^{-2}$ mm., Table VII shows the diminishing importance of the impedance effect as the water vapour concentration increases. This is to be expected, as the result of two factors both operating in the same direction. The concentration of adsorbed molecules in the interface corresponds to some unknown effective concentration of free water molecules in that place. The excess of this concentration over what is due to the presence of water vapour outside is proportional to the reaction rate per unit area of interface, and hence decreases as this rate decreases with increase in the external concentration. But besides this there is the fact that the *additional* lowering produced by a given excess concentration also decreases with increase of total concentration in the interface ; thus Table V shows that when the external concentration is zero the lowering of rate due to an added $0 \cdot 5 \,.\, 10^{-2}$ mm. of water vapour is of the order of 40 per cent., whereas when the external partial pressure is already $4 \,.\, 10^{-2}$ mm. the additional $0 \cdot 5 \,.\, 10^{-2}$ mm. only produces a lowering of about 5 per cent. of the rate at that water vapour pressure.

Discussion.

Fig. 2 shows the logarithms of the rates plotted against reciprocals of the absolute temperatures. The points not enclosed in circles or squares show the effect of the self-cooling in vacuum, which above about 20° produces an entirely erroneous temperature coefficient. The heavy line is the best straight line* drawn through the points enclosed by circles and squares, which represent respectively the corrected temperatures for the vacuum experiments and the experiments with hydrogen present, obtained by the "static" method.

The line marked G.T. is the mean line given by Garner and Tanner (*loc. cit.*) covering the range over which they measured the formation of the monohydrate. Their results are a little lower than ours, probably partly because they have not been extrapolated back to the initial rate in any systematic way and partly because of a little more self-cooling due to the proximity of a liquid air trap. Making allowance for this, the agreement of our values with those of Garner and Tanner is as good as could be expected, and the mean slopes of the lines would be the same over the common temperature range. Since the experimental arrangement of Garner and Tanner was obviously an extremely efficient one for trapping the water molecules leaving the surface of the crystal, the fact that their rates are a little lower than ours gives us confidence that no disturbance was caused in our experiments through failure to absorb the water vapour sufficiently quickly.

The absolute reaction velocity coefficient is given by

$$\mathrm{Log}_{10}\,\mathrm{K} = 12 \cdot 112 - \frac{3982}{\mathrm{T}}$$

the units of K being milligrams H_2O per square centimetre per minute. The empirical energy of activation is 18,250 cal. per gram molecule of H_2O.

The most important question concerning the experimental results is whether the impedance effect of the lower hydrate is effectively eliminated by the extrapolation method. It might at first seem that since the mono-hydrate is present in an extremely finely divided state it would set a lower limit to the concentration of water vapour in the immediate neighbourhood of the interface, namely, its own vapour pressure in respect of the anhydrous phase, which amounts to about 0·1 mm. at 43°. This, however, is not the case; we found that a pseudomorph of one of the crystals used after being one-fifth dehydrated to the anhydrous phase only lost 0·00015 mgm. per minute at 43°, as against 0·280 from a square centimetre of the penta-hydrate interface. The fact that the mono-hydrate has this vapour pressure is therefore not significant for the decomposition of the penta-hydrate.

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* It is not implied that there is any theoretical reason for doing so ; but the straight line represents the points over this range within the limits of error.

Garner and Tanner suggest that the water vapour pressure in the reaction zone inside the crystal can rise to a value exceeding the dissociation pressure of the tri-hydrate, because this hydrate was formed instead of the mono-hydrate at 56. They consider, therefore, that there is always present a serious complication through what we have termed the impedance effect. But the dissociation pressure of the tri-hydrate mono-hydrate system is about 45 mm. at this temperature, and in view of the effect of even small pressures in depressing the rate it is quite impossible that a pressure of this order is present. This question of the reason for the formation of the tri-hydrate is not further discussed here, because the experiments of Hume and Colvin are more directly concerned with it.

In the experiment at 22·25° in the presence of hydrogen (Table I) the rate per unit interface area falls off between 2 per cent. and 40 per cent., decomposition by only 25 per cent., while the thickness through which the water vapour must diffuse increases 15-fold. It seems impossible that in the initial 2 per cent. there can be any abnormally large decrease in rate.*

Moreover, if we compare the numerical results obtained by Garner and Tanner, by Hume and Colvin, and by ourselves, using crystals of quite different sizes,

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* The experiments with added water vapour indicate that the lowering of the rate becomes linear for quite small pressures. Assuming that the mono-hydrate layer behaves simply as a porous medium with a resistance proportional to its thickness and inversely to its area, then, combining the expression for the interfacial concentration of water molecules as a function of α with a linear relationship between interfacial concentration and lowering of rate, we derive the result that

$$\frac{(1-\alpha)^{2/3}-\rho}{\rho\{1-(1-\alpha)^{1/3}\}}=C,$$

where C is a constant dependent upon temperature and the dimensions of the crystal used. ρ is the quotient of the rate at α divided by the extrapolated rate corresponding to $\alpha =$ zero. In practice the rate decreases rather *less*, not more rapidly than this view would suggest.

we find for the mean rates, at the temperature at which Hume and Colvin worked (20) :—

	Rate.	Average weight, mgm.
Garner and Tanner	0·250	320
Hume and Colvin	0·021	0·00253
Smith and Topley	0·027	50

Hume and Colvin used a sample consisting of a very large number of small crystals. The impedance effect would be least in Hume and Colvin's experiments and greatest in Garner and Tanner's, but the results are not in this order. Hume and Colvin found no falling off in the rate per unit interface area between 12 per cent. (where the maximum rate is reached at the end of the accelerating portion of the reaction) and 80 per cent.

It is interesting to note that the molecular volume of the mono-hydrate is 54·3 and that of the penta-hydrate 109·1, so that the mono-hydrate forming the pseudomorph of the original crystal must have at least half its volume composed of inter-granular spaces, so that the apparent ease of escape of water molecules which has been remarked by several workers is perhaps not surprising.

Summary.

Difficulties affecting the measurement of the rate of dehydration of salt hydrates are discussed. An apparatus is described designed to take account of these difficulties, and to allow the study of the influence of small partial pressures of different gases, in particular water vapour.

The rate of dehydration of copper sulphate penta-hydrate to the mono-hydrate has been studied over the temperature range 0° to 43°. The sensitivity to small water vapour concentrations is very variable with temperature; detailed measurements have been made between 20° and 35°.

The absolute rate of the decomposition reaction, unaffected by the reverse reaction or by water vapour " poisoning " of the interface, is expressed by

$$\mathrm{Log}_{10} \mathrm{K} = 12{\cdot}112 - \frac{3982}{\mathrm{T}},$$

where K is in milligrams per square centimetre per minute.

We have great pleasure in expressing our thanks to Mr. A. B. D. Cassie for his assistance, and to the Department of Scientific and Industrial Research for a grant to one of us (M.L.S.).

Studies of Gas-Solid Equilibria. Part III.—*Pressure-Concentration Equilibria between Silica Gel and* (*a*) *Water,* (*b*) *Ethyl Alcohol, directly determined under Isothermal Conditions.*

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In this part of the work a thorough examination has been made of the pressure-concentration equilibria between silica gel and (*a*) water, (*b*) ethyl alcohol, at several temperatures, under strictly isothermal conditions and covering the whole range of concentrations possible. " Ascending " and " descending " pressure-concentration isothermals have been drawn from these direct measurements and the reversibility of the systems carefully investigated.

The experimental procedure was exactly the same as that used and described in Part II* of this work, except that the " cut-off " between the gel system and the calibrated reservoir was heated by a toluene vapour jacket instead of a steam jacket. In these and subsequent experiments the apparatus was constructed of Pyrex glass, with the exception of the calibrated reservoir which was made of ordinary soft glass and sealed to the rest by a graded Pyrex soft glass fused joint.

All evacuations were carried out by means of a Gaede two-stage mercury vapour pump with a Gaede rotary oil pump as a backing pump. A McLeod gauge was included in the evacuating system.

The System Water-Silica Gel.

The silica gel (in the form of small granules) was from the same batch as that used in Parts I and II of this work. It was activated and weighed *in vacuo* as described in Part I.†

Pure water was prepared by distillation, *in vacuo*, from an aqueous solution of pure baryta as described by Lambert and Thomson.‡

Since early experiments on the water-silica gel system showed marked differences in behaviour from the analogous system benzene-silica gel (*vide* Part II, *loc. cit.*), the system has been investigated over a long period, and with different samples of gel, so that no doubt should remain concerning its peculiar character.

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* 'Proc. Roy. Soc.,' A, vol. 122, p. 497 (1929).

† 'Proc. Roy. Soc.,' A, vol. 117, p. 183 (1927).

‡ 'J. Chem. Soc. Trans.,' vol. 97, p. 2426 (1910).

These experiments have shown that the water-silica gel system is quite definitely peculiar in the following respects:—

(i) A pressure-concentration isothermal drawn from the values obtained in any one experiment, on the water-silica gel system, is not reproducible. Any repetition of an experiment, on the same sample of gel and under exactly the same experimental conditions, leads to new values, the equilibrium pressures being higher than they were (at the same concentration) in the preceding experiment. *Each successive new experiment on the same sample of gel leads to a shift of the pressure-concentration isothermal towards the pressure axis.*

(ii) A pressure-concentration isothermal for the water-silica gel system cannot be followed experimentally up to the saturation pressure of water vapour at the temperature of the system. An isothermal always flattens out at a pressure slightly below the saturation pressure and then very slowly rises towards that pressure.

A period over which very small increases of water concentration have led to very rapid rises in the equilibrium pressures, is followed, in all cases, as the system closely approaches saturation, by a period over which relatively large amounts of water can be added while the equilibrium pressure rises with extreme slowness towards the vapour pressure of pure water.

(iii) A pressure-concentration isothermal for the water-silica gel system is not reversible. Over a range intermediate between high and low water concentrations the " descending " isothermal shows a wide divergence from the " ascending " isothermal and produces hysteresis; further, the lack of coincidence of " ascending " and " descending " isothermals is not always confined to the range of water concentrations covered by the hysteresis region.

In all these respects the water-silica gel system has been shown to behave quite differently from the analogous benzene-silica gel and alcohol-silica gel systems.

The time taken for the establishment of an equilibrium point, after either the addition of water to the system or the withdrawal of water from it, was usually about 3 hours over those ranges of concentration when the " ascending " and " descending " isothermals were coincident; no markedly longer period was required for the establishment of an equilibrium point over those ranges of concentration when there was a divergence between the " ascending " and " descending " isothermals.

Most of the experiments made on this system were carried out at 60° C. and 70° C. Only one experiment, with a fresh sample of gel, was carried out at 50° C. and the results are used (in Graph V) for a comparison of the pressure-concentration isothermals of the three analogous systems—

(*a*) Benzene-silica gel;
(*b*) Ethyl alcohol-silica gel;
(*c*) Water-silica gel.

In Tables A and B below, the results are given of five consecutive experiments carried out at 60° C. and 70° C. with one and the same sample of gel. In this series of experiments no attempt was made to investigate the equilibrium at high concentrations of water since it was thought, at the time, that the non-reproducibility of equilibrium points in earlier consecutive experiments might possibly have been due to a sort of " water-logging " of the gel. The results of this series of experiments clearly showed that there was no justification for this supposition and that the non-reproducibility of equilibrium points in consecutive experiments was a characteristic peculiarity of the system. These results, and the isothermals drawn from them, are therefore typical of the system.

The equilibrium points in each experiment are numbered in the order in which they were determined and the results are plotted in Graph I, Curves I to V. All pressures are given in centimetres of mercury at 0° C. The water-content of the gel is expressed in grams of water per gram of gel.

Note.—The water which forms part of the gel structure and which is present in the activated and evacuated gel, is not taken into account.

The results of the first two experiments carried out at 60° C., immediately after one another, are plotted in Curves I and II. Two similar consecutive experiments were then carried out at 70° C. and the results are plotted in Curves IV and V. Curve III represents the results of a final experiment carried out at 60° C.

The weight (*in vacuo*) of the silica gel used in this series of experiments was 11·610 grams.

Table A.—Temperature 60° C.

1st and 2nd Experiments.

No.	Concentration of water.	Pressure.	No.	Concentration of water.	Pressure.
1	0·0157	0·140	15	0·1633	5·220
2	0·0477	0·840	16	0·1788	6·115
3	0·0890	2·120	17	0·1940	7·815
4	0·1215	3·290	18	0·2056	10·170
5	0·1563	4·910	19	0·2092	11·970
6	0·1776	5·975	20	0·2178	14·62
7	0·1981	8·090	21	0·2156	13·6
8	0·2077	9·965	22	0·2068	10·880
9	0·2166	12·910	23	0·1993	8·575
10	0·2059	9·245	24	0·1931	7·025
11	0·1981	7·520	25	0·1901	6·690
12	0·1894	6·275	26	0·1884	6·430
13	0·1858	6·150	27	0·1847	6·200
14	0·1801	5·870	28	0·1739	5·870

1st experiment—
“ Ascending ” points 1 to 9 .... } Curve I.
“ Descending ” points 10 to 15 .... }

2nd experiment—
“ Ascending ” points 16 to 20............ } Curve II.
“ Descending ” points 21 to 28 .... }

5th Experiment.

No.	Concentration of water.	Pressure.	No.	Concentration of water.	Pressure.
1	0·0557	1·205	10	0·1705	6·465
2	0·1137	4·040	11	0·1684	6·240
3	0·1523	6·015	12	0·1670	6·170
4	0·1695	7·420	13	0·1630	6·060
5	0·1778	8·645	14	0·1603	6·010
6	0·1851	10·940	15	0·1525	5·785
7	0·1907	13·420	16	0·1470	5·665
8	0·1810	9·45	17	0·1416	5·415
9	0·1755	7·740	18	0·1293	4·865

“ Ascending ” points 1 to 7............ } Curve III.
“ Descending ” points 8 to 18............ }

Table B.—Temperature 70° C.

3rd and 4th Experiments.

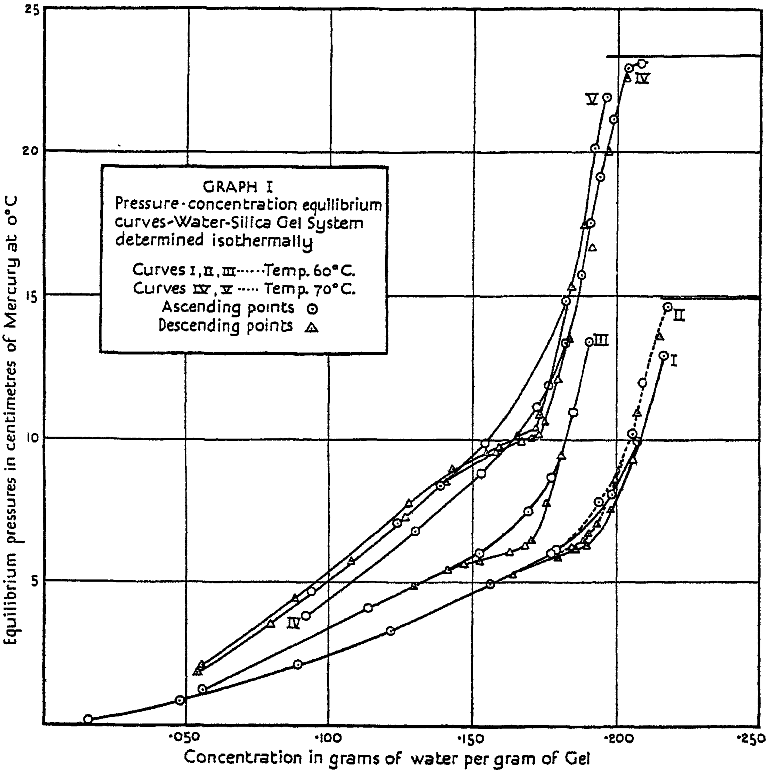
No.	Concentration of water.	Pressure.	No.	Concentration of water.	Pressure.
1	0·0915	3·870	27	0·0796	3·525
2	0·1294	6·730	28	0·0539	1·825
3	0·1529	8·805	29	0·0936	4·650
4	0·1724	11·110	30	0·1235	7·055
5	0·1766	11·850	31	0·1389	8·380
6	0·1827	13·345	32	0·1544	9·850
7	0·1878	15·720	33	0·1835	14·825
8	0·1911	17·58	34	0·1926	20·17
9	0·1942	19·120	35	0·1962	21·97
10	0·1986	21·20	36	0·1886	17·525
11	0·2040	22·95	37	0·1847	15·35
12	0·2071	23·105	38	0·1774	11·970
13	0·2034	22·635	39	0·1737	10·870
14	0·1970	20·050	40	0·1724	10·375
15	0·1916	16·70	41	0·1708	10·175
16	0·1835	13·550	42	0·1685	10·180
17	0·1794	12·10	43	0·1678	10·120
18	0·1749	10·585	44	0·1661	10·120
19	0·1733	10·220	45	0·1630	9·955
20	0·1710	10·020	46	0·1612	9·895
21	0·1688	10·015	47	0·1594	9·73
22	0·1674	9·910	48	0·1431	8·980
23	0·1587	9·555	49	0·1274	7·750
24	0·1407	8·485	50	0·0879	4·465
25	0·1265	7·190	51	0·0557	2·050
26	0·1075	5·740			

3rd experiment—
"Ascending" points 1 to 12 .... } Curve IV.
"Descending" points 13 to 28 .... }

4th experiment—
"Ascending" points 29 to 35............ } Curve V.
"Descending" points 36 to 51 .... }

The shift of the pressure-concentration isothermals towards the pressure axis is clearly shown in Curves I and II (at 60° C.) and Curves IV and V (at 70° C.) in experiments following immediately after one another at the same temperature. Curve III—the 60° C. isothermal, drawn from the final experiment, conducted after two experiments at the higher temperature—shows how this shift has become very marked throughout the whole course of the curve.

Hysteresis is shown by all the pressure-concentration isothermals and it is to be noticed that the hysteresis area seems to increase in consecutive experiments carried out at the same temperature.



It is to be noticed, further, that the first " descending " isothermal (Curve IV) at 70° C. does not join the original " ascending " isothermal, but crosses over it and forms a new curve, which is retraced, up to the hysteresis area, by the second " ascending " isothermal. The failure of the " descending " isothermal to coincide, at low water concentration, with the " ascending " isothermal is again shown (Curve V) in the second experiment at 70° C.

In these experiments the temperature of the system was maintained strictly at the chosen value throughout each experiment and there were no interruptions in the smooth additions of water to the system or the smooth withdrawals of water from it. Separate experiments were made to study the effects of departures from this procedure by—

(*a*) Temporary and sudden alterations in the temperature (both to higher and to lower values) followed by restoration to the original controlled temperature;

(*b*) Occasional interruptions in the smooth addition or withdrawal of water.

Such departures from the usual procedure produced no alterations in the equilibrium pressures except over those ranges of concentration covered by the hysteresis region. In this region new equilibrium pressures were obtained which fell within the hysteresis area. The effects of these departures from the usual procedure were thus the same as were observed in the benzene-ferric oxide gel system (Part II, *loc. cit.*) and in the hydrogen-palladium system.*

It was later found that if, after the establishment of an equilibrium point at 60° C., the temperature of the system was *very slowly* raised to 70° C., and subsequently *very slowly* reduced to 60° C., there was no appreciable alteration in the original equilibrium pressure. This is illustrated by the following figures :—

Original pressure at 60° C.	Final pressure at 60° C. after slow alteration to 70° C. and slow return to 60° C.
cm.	cm.
6·40	6·39
6·30	6·31
6·15	6·18
6·05	6·10
6·00	5·99

A similar very slow reduction of the temperature to 60° C., after the establishment of an equilibrium point at 70° C., followed by a very slow raising of the temperature back to 70° C., was found to produce no appreciable alteration in the original pressure.

Note.—These slow alterations in the temperature were easily effected by the withdrawal of mercury from (or the addition of mercury to) the manostat controlling the pressure inside the vapour bath surrounding the system (*vide* Part II, *loc. cit.*).

Since, owing to the shift which invariably occurred between the determination of successive isothermals, there was no hope of getting really comparable results for two different temperatures by the ordinary procedure, an attempt was made to obtain comparable equilibrium points at 60° C. and 70° C. in one and the same experiment, using the procedure described above.

In this way 32 equilibrium points were determined at the two temperatures, covering the range of water concentrations within which previous experiments had shown hysteresis to occur. The results are given in Table C below and they are plotted in Graph II. The points are numbered, both in the table and in the graph, in the order in which they were obtained.

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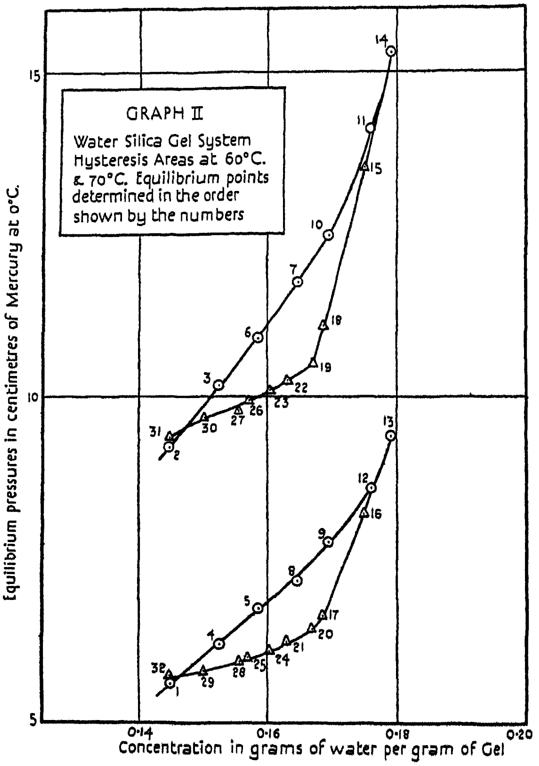
* ‘Proc. Roy. Soc.,’ A, vol. 108, p. 456 (1925).

It is not claimed that these values afford a very strict comparison of the behaviour of the water-silica gel system at 60° C. and 70° C. They are, however, the only results obtained which have any claim to show the comparative behaviour of the system at two different temperatures.

Table C.—Temperatures 60° C. and 70° C.

No.	Concentration of water.	Pressure at 60° C.	Pressure at 70° C.
1	0·1448	5·600	—
2	—	—	9·230
3	0·1526	—	10·170
4	—	6·195	—
5	0·1586	6·745	—
6	—	—	10·935
7	0·1647	—	11·785
8	—	7·165	—
9	0·1695	7·770	—
10	—	—	12·495
11	0·1761	—	14·12
12	—	8·60	—
13	0·1789	9·43	—
14	—	—	15·310
15	0·1748	—	13·520
16	—	8·21	—
17	0·1685	6·63	—
18	—	—	11·070
19	0·1670	—	10·52
20	—	6·40	—
21	0·1631	6·24	—
22	—	—	10·25
23	0·1603	—	10·105
24	—	6·10	—
25	0·1569	6·00	—
26	—	—	9·94
27	0·1556	—	9·77
28	—	5·93	—
29	0·1501	5·79	—
30	—	—	9·68
31	0·1448	—	9·38
32	—	5·71	—



Behaviour of the System near the Saturation Pressure.

The remarkable behaviour of the water-silica gel system at water concentrations closely approaching saturation was very carefully investigated at 50° C., 60° C. and 70° C. At none of these temperatures could the pressure-concentration isothermals be followed, experimentally, up to the saturation pressure of water for the particular temperature. The isothermals, after rising sharply towards the saturation pressure, always flattened out when the pressure came within a few millimetres of the saturation pressure and then very slowly rose towards that value; the addition of comparatively large quantities of water, at this stage, produced very small increases in the equilibrium pressure.

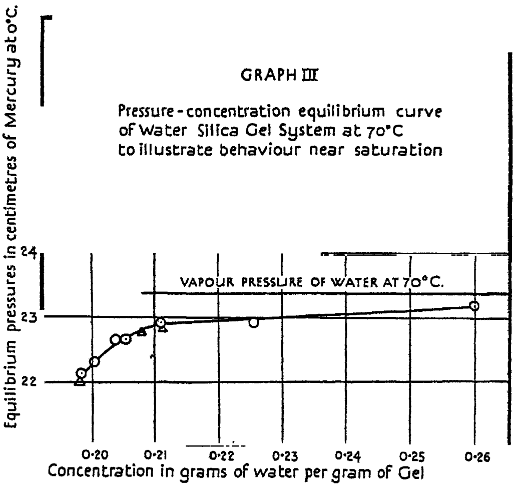
When water was distilled into the system under these conditions, liquid water was seen to condense on the mercury in the manometer and the pressure became exactly equal to the vapour pressure of pure water. This liquid water slowly distilled (over a period of several hours, depending on its amount) on to the gel and the pressure in the system then fell. At no time was liquid water seen in contact with the gel itself and the appearance of the gel showed no visible change throughout the whole range of experiment.

In Table D below equilibrium points are given for the system at water concentrations close to saturation at 70° C. (these results are typical of the experiments at all the temperatures investigated). The equilibrium points are numbered in the order in which they were determined and they are plotted in Graph III.

Table D.—Temperature 70° C.

No.	Concentration of water.	Pressure.	No.	Concentration of water.	Pressure.
1	0·1985	22·120	6	0·2256	22·930
2	0·2006	22·300	7	0·2607	23·21
3	0·2038	22·660	8	0·2111	22·820
4	0·2055	22·650	9	0·2080	22·75
5	0·2111	22·880	10	0·1984	21·970

" Ascending " points—1 to 7.
" Descending " points—8 to 10.



The System Ethyl Alcohol-Silica Gel.

The silica gel used in the experiments on this system was the same as that used in the final series of experiments (Tables A and B) on the water-silica gel system. After the last experiment at 60° C. the calibrated water reservoir was surrounded by ice, while the gel system was kept at 60° C., until all the water removable under these conditions had distilled from the gel. Dry air was then allowed to enter the whole apparatus and it was connected up to the mercury pump through a large tube containing phosphorus pentoxide.

The gel was then heated to 148° C. (by boiling amyl acetate in the vapour bath surrounding the gel system) and kept continuously at this temperature for several days and nights. During the daytime the mercury vapour pump was kept running. The gel was thus made to lose the water removable under the original conditions of activation and was therefore restored, approximately, to its original condition.

The ethyl alcohol used was kindly supplied by the Balliol College Laboratory and was of the high degree of purity employed for electrical conductivity work in that laboratory. It was finally distilled, *in vacuo*, over anhydrous copper sulphate and collected in sealed tubes for use according to our usual procedure.

Five experiments were carried out on this system, the experimental procedure being precisely the same as that used in the earlier work. The system was studied in consecutive experiments at 60° C., 70° C., 50° C., and 40° C., a final (repetition) experiment being done at 60° C. The results are given in Table E below. Pressures are expressed in centimetres of mercury at 0° C. and the concentration of alcohol in the system is expressed in grams of alcohol per gram of gel.

The results are plotted in Graph IV.

Table E.

1st Experiment. Temperature 60° C.

No.	Concentration of alcohol.	Pressure.	No.	Concentration of alcohol.	Pressure.
1	0·0250	0·060	14	0·1574	19·94
2	0·051	0·095	15	0·1555	18·24
3	0·0780	0·270	16	0·1533	17·09
4	0·0880	0·460	17	0·1515	16·26
5	0·0996	0·890	18	0·1489	14·98
6	0·1147	3·115	19	0·1452	13·65
7	0·1252	6·490	20	0·1407	11·98
8	0·1486	14·92	21	0·1362	10·385
9	0·1562	18·47	22	0·1331	9·195
10	0·1617	27·7	23	0·1285	7·445
11	0·1662	34·92	24	0·1208	4·905
12	0·1632	32·65	25	0·1098	2·095
13	0·1602	25·57			

" Ascending " points—1 to 11 .... } Curve III.
" Descending " points—12 to 25 .... }

Table E—(continued).

5th Experiment. Repetition at Temperature 60° C.

No.	Concentration of alcohol.	Pressure.	No.	Concentration of alcohol.	Pressure.
1	0·1678	35·12	7	0·1078	1·42
2	0·1621	22·77	8	0·1275	6·60
3	0·1576	17·80	9	0·1501	14·57
4	0·1379	10·29	10	0·1643	28·20
5	0·1236	5·00	11	0·1672	34·5
6	0·1150	2·49	12	0·1531	15·58

“ Descending ” points—1 to 7 and 12 .... } Curve III
“ Ascending ” points—8 to 11 .... } (dotted).

2nd Experiment. Temperature 70° C.

No.	Concentration of alcohol.	Pressure.	No.	Concentration of alcohol.	Pressure.
1	0·1662	53·27	11	0·1052	2·665
2	0·1621	44·7	12	0·0970	1·440
3	0·1607	39·50	13	0·1076	3·200
4	0·1499	24·70	14	0·1160	5·91
5	0·1476	23·31	15	0·1267	11·56
6	0·1418	19·83	16	0·1384	18·18
7	0·1321	14·88	17	0·1513	25·93
8	0·1266	11·66	18	0·1544	28·47
9	0·1214	8·665	19	0·1582	32·97
10	0·1134	4·960			

“ Descending ” points—1 to 12 .... } Curve IV.
“ Ascending ” points—13 to 19 .... }

3rd Experiment. Temperature 50° C.

No.	Concentration of alcohol.	Pressure.	No.	Concentration of alcohol.	Pressure.
1	0·1006	0·485	11	0·1627	15·135
2	0·1033	0·525	12	0·1638	18·01
3	0·1101	0·941	13	0·1666	22·17
4	0·1173	1·875	14	0·1645	18·96
5	0·1236	2·975	15	0·1593	11·81
6	0·1395	6·605	16	0·1579	11·11
7	0·1460	7·870	17	0·1445	7·54
8	0·1506	8·97	18	0·1276	3·87
9	0·1559	10·480	19	0·1654	21·94
10	0·1621	14·42			

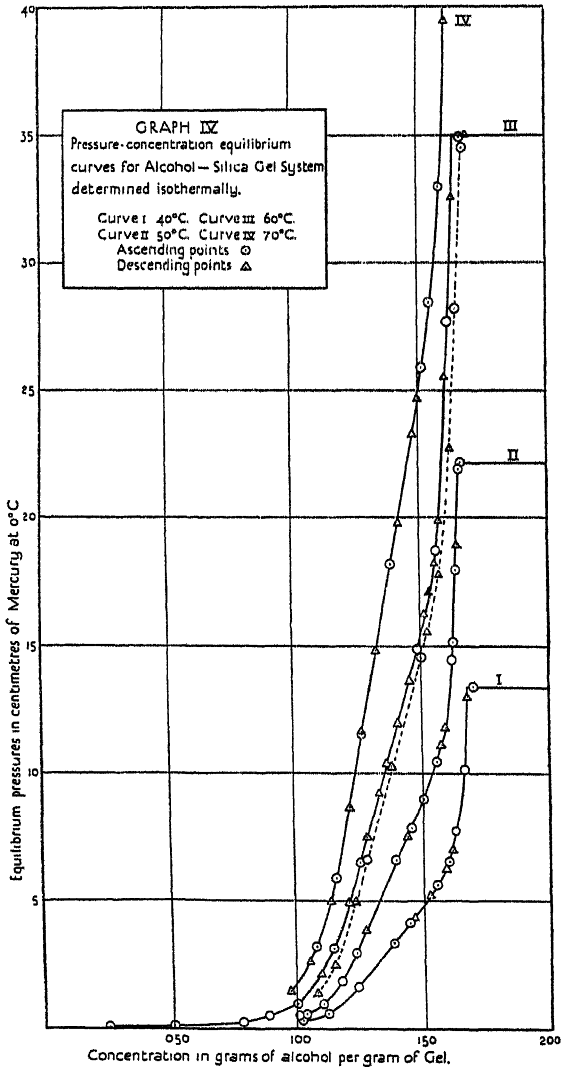
“ Ascending ” points—1 to 13 and 19 .... } Curve II.
“ Descending ” points—14 to 18 .... }

Table E—(continued).

4th Experiment. Temperature 40° C.

No.	Concentration of alcohol.	Pressure.	No.	Concentration of alcohol.	Pressure.
1	0·1016	0·300	9	0·1668	10·120
2	0·1123	0·550	10	0·1701	13·4
3	0·1241	1·625	11	0·1679	12·980
4	0·1382	3·325	12	0·1619	6·98
5	0·1443	4·125	13	0·1590	6·24
6	0·1555	5·630	14	0·1527	5·195
7	0·1602	6·570	15	0·1464	4·325
8	0·1631	7·775			

"Ascending" points—1 to 10 .... } Curve I.
"Descending" points—11 to 15 .... }



The early results obtained in the study of this system at 60° C. were somewhat irregular and the equilibrium points on the first "ascending" isothermal did not fall on a smooth curve. When the gel was nearly saturated with alcohol it had to be left during a vacation of about 1 month and, on the resumption of the work, the system appeared to have "settled down." The pressure reached equilibrium in about 1 hour after the addition or withdrawal of alcohol and all the equilibrium points fell on a smooth curve. A completely reversible pressure-concentration isothermal (Curve III) was obtained over the whole range of possible concentrations, the "ascending" and "descending" isothermals being coincident throughout and showing no trace of hysteresis. Temporary and sudden alterations in the temperature of the system, followed by restoration to the original controlled temperature, produced no alteration in the equilibrium pressure; occasional departures from the smooth addition or withdrawal of alcohol also produced no equilibrium points falling off the curve.

In the second experiment, carried out at 70° C. (Curve IV), no irregularity in the behaviour of the system was noticed, but, in the third experiment at 50° C. (Curve II) and the fourth experiment at 40° C. (Curve I), there was in each case an initial irregularity and a short "settling down" period required before completely repeatable and reversible results could be registered. During these short periods of uncertainty the pressures registered were always slightly higher than those subsequently obtained.

The fifth experiment—a repetition of the first experiment at 60° C.—gave results in which the equilibrium pressures were throughout lower than those registered at the same alcohol concentrations in the first experiment. The equilibrium points in this fifth experiment were completely reversible and the new "ascending" and "descending" isothermals (dotted Curve III) were coincident throughout the whole range of concentrations. *A shift of the isothermal away from the pressure axis had thus taken place.*

The purity of the gaseous phase and the accuracy of the technique in this series of experiments is shown by the very close agreement between the saturation pressures recorded and the vapour pressures of pure alcohol:—

Temperature.	Observed saturation pressure.	Vapour pressure of pure ethyl alcohol.	
		Ramsay and Young.	Merriman.
° C.	cm.	cm.	cm.
40	13·40	13·34	13·49
50	22·17	21·98	22·22
60	35·12	35·02	35·27

The system ethyl alcohol-silica gel thus behaves like the system benzene-silica gel (*vide* Part II, *loc. cit.*) in giving pressure-concentration isothermals which show no hysteresis. The equilibrium in both systems is reversible throughout the whole range of concentrations, and in both systems the equilibrium pressures rise (with increasing concentrations) smoothly and regularly up to saturation pressures equal to the vapour pressures of the pure liquids themselves.

There is, however, in the case of the alcohol-silica gel system a tendency to irregularity in behaviour in the early stages of an experiment and there is, further, a tendency to a shift of the pressure-concentration isothermal away from the pressure axis.

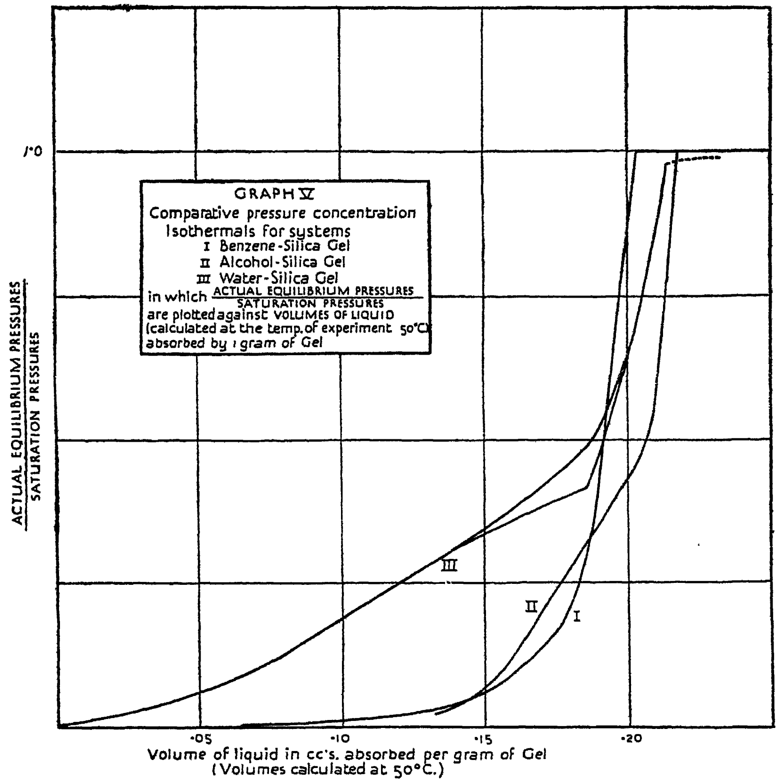
It is significant that no such irregularities are found in the analogous benzene-silica gel system which shows a certainty of behaviour and a high degree of epeatability throughout a long series of experiments at different temperatures.

Comparison of the Three Systems—(a) Water-Silica Gel; (b) Benzene-Silica Gel; (c) Ethyl Alcohol-Silica Gel.

For purposes of comparison the equilibrium pressures of the three systems, at 50° C., have been reduced to the same pressure scale by dividing the pressures by the saturation pressures in each case; the relative pressures so obtained have been plotted, in Graph V, against the volumes of the three liquids absorbed per gram of gel (these volumes being calculated at 50° C.).

The alcohol and benzene isothermals reach saturation pressure when 0·218 c.c. and 0·204 c.c. of the respective liquids have been absorbed per gram of gel; the water isothermal bends over and begins to behave abnormally (shown by the dotted portion of the curve) when 0·214 c.c. of water have been absorbed per gram of gel. The volumes of the three liquids absorbed by one gram of gel are thus approximately equal when the systems are close to saturation.

The water isothermal is obviously quite different in character from the benzene and alcohol isothermals. Apart from the fact that there is marked hysteresis between the "ascending" and "descending" isothermals, over a considerable range of concentrations, and that there is abnormality of behaviour close to saturation, the water isothermal rises very much more steeply from the concentration axis than the benzene and alcohol isothermals. When the concentration of water, in the water-silica gel system, has reached a value approximately two-thirds of the saturation value, the equilibrium pressure is nearly one-third of the saturation pressure; at the same concen-



trations in the benzene-silica gel and alcohol-silica gel systems, the equilibrium pressures are only about one-twentieth of the saturation pressures.

The benzene and alcohol isothermals are alike in that they show no trace of hysteresis, are completely reversible over the whole range of concentrations, and pass smoothly up to saturation pressures equal to the vapour pressures of the pure liquids.

There is, however, a striking difference in the shapes of the two isothermals. They are alike in rising very slowly from the concentration axis until the concentrations approach two-thirds saturation value; but, while the benzene isothermal shows no sudden change of direction from this point up to the saturation value, the alcohol isothermal makes a rather sudden turn upwards and becomes linear in character for a considerable period.

The non-reproducibility, in successive experiments, of the equilibrium points in the water-silica gel system, and the persistent shift of the pressure-concentration isothermals towards the pressure axis, might possibly be explained by volume changes in the gel itself.

A long experience of many similar gels goes to show that, after preparation by precipitation, washing and subsequent drying at room temperature, they have practically no absorptive power for gases and vapours.

At this stage of its preparation, a gel might be quite brittle and hard, show a highly lustrous fracture and be transparent in thin layers; it still contains a large percentage weight of water, most of which must be removed before the gel can attain to its optimum activity or power to absorb gases and vapours.

A gel which has been thoroughly dried at room temperature, can be made to lose this excess of water and be raised to its optimum activity by heating in a current of dry air, or *in vacuo*, for a sufficient length of time at the proper temperature (the temperature differs widely for different gels). The loss of water, and consequent activation of the gel, is accompanied by a marked decrease in its volume but, apart from this shrinkage, the outward appearance of the gel may show no change in spite of the loss of much water. Judging from measurements of the apparent density of gel particles during this activation process, the shrinkage of the gel appears to continue right down to the final stages of the operation.

It is not unreasonable to suppose that the replacement of water in the gel leads to a reversal of this effect—that the absorption of water by the activated gel causes it to swell to some extent; but the swelling would be completely reversed, and the gel restored to its original activity, if the added water were again removed under the precise conditions employed in the original activation process.

Note.—Evidence of the validity of this contention is afforded from a consideration of the comparative pressure-concentration isothermals in Graph V. The alcohol isothermal was drawn from results obtained in experiments with a sample of silica gel which had previously been used in experiments on the water-gel system. In these experiments, the absorptive capacity of the gel, after five experiments with water, had decreased about 10 per cent. (compare Curves I and III in Graph I). But the slow removal of most of the water at 60° C., followed by heating for several days, *in vacuo*, at 148° C. (the original conditions of activation) fully restored the absorptive capacity of the gel as shown by the volume of alcohol taken up by 1 gram of gel.

It is, however, probable that, under the conditions of our experiments on the water-silica gel system (the gel being maintained at 60° C., or 70° C., in an atmosphere of water vapour), the process of shrinkage of the gel, after the reduction of its water-content, would be much slower than the process of swelling of the gel after an increase of its water-content. This would have the result that, after the first experiment on a sample of gel, each subsequent experiment would be carried out on a gel of slightly greater volume and less absorptive power.

If the above assumptions are valid, we have a reasonable explanation of the persistent shift of the pressure-concentration isothermals towards the pressure axis, in successive experiments carried out on the water-silica gel system; we also have an explanation of the curious behaviour of the "descending" isothermals, at low water concentrations, in the experiments at 70° C. (see Curves IV and V, Graph I).

The assumption of changes of volume with the water-content of the gel, affords no explanation of the existence of hysteresis phenomena in the water-silica gel system (its effect would be actually to decrease the hysteresis area); but it provides a possible explanation of the irregular behaviour shown by the alcohol-silica gel system—the necessity for a "settling down" period before reliable and repeatable results are possible—and of the tendency to a slight shift of the pressure-concentration isothermals in the opposite direction—away from the pressure axis. It is known that pure alcohol has a great affinity for small quantities of water and, when alcohol is absorbed by a gel, it may exercise its attractive power on that water which remains in the gel after it has been activated; the effect would be to cause a slight shrinkage of the gel with consequent increased activity. A new experiment, involving a change of temperature, on the alcohol-silica gel system, would also involve a re-adjustment of the effect of the alcohol on the residual water and so cause the uncertainty of behaviour which was noticed in the early stages of an experiment. The cumulative effect of the dehydrating action of the alcohol would raise the absorptive power of the gel and so afford an explanation of the shift of the 60° C. isothermal noticed in the last experiment on the alcohol-silica gel system.

An outstanding feature of the experiments, described in Part II (*loc. cit.*), on the benzene-silica gel and benzene-ferric oxide gel systems, is the high degree of reproducibility of the results of long series of experiments and the entire freedom from irregularity in behaviour. It is possible, in the light of the views expressed above, that the explanation of the smooth behaviour of benzene, in its relations with dehydrated gels, is to be found in its lack of affinity for water.

Note.—In Part IV of this work, which deals with the absorption of vapours on two kinds of ferric oxide gel, benzene has been found to differ from water and alcohol in the same manner.

No satisfactory explanation can be offered of the anomalous behaviour of the water-silica gel system in the neighbourhood of saturation. It is well known that there is great difficulty in removing all traces of soluble salts in the preparation of gels; although a water extract of the silica gel failed to give any chemical test for chloride there is no doubt that traces of hydrochloric acid are produced when the gel is heated to a high temperature, *in vacuo*, in a quartz tube. In order to account for the lowering of vapour pressure observed in these experiments, if the effect is due to a solute in the absorbed water, it is necessary to assume that the silica gel contains more than one-quarter of 1 per cent. of sodium chloride.

Summary.

The pressure-concentration equilibria between silica gel and (*a*) water, (*b*) ethyl alcohol, have been determined under isothermal conditions and at several temperatures.

It has been shown that the water-silica gel system is definitely peculiar in behaviour and that it is markedly different from the benzene-silica gel and the alcohol-silica gel systems.

The water isothermals show hysteresis phenomena and they rise very much more steeply from the concentration axis than the benzene and alcohol isothermals; they are not reproducible in successive experiments and show a persistent shift towards the pressure axis; they cannot be followed experimentally up to the saturation pressures of pure water at the temperatures investigated.

The pressure-concentration isothermals for the alcohol-silica gel system have been shown to resemble those for the benzene-silica gel system described in Part II, being reversible, showing no hysteresis phenomena, and giving saturation pressures equal to those of pure ethyl alcohol; but the alcohol isothermals differ in shape from the benzene isothermals and the alcohol-silica gel system displays irregularities in behaviour not shown by the benzene-silica gel system.

A partial explanation of the results is put forward; this is based on the assumption that the volume of the gel changes with its water-content—that it is, in fact, not strictly non-elastic.

Some of the apparatus used in this work was purchased out of a grant made by the Imperial Chemical Industries, Ltd.; this assistance is acknowledged with much gratitude.

The Normal Vibrations of Carbonate and Nitrate Ions.

By A. C. Menzies, University College, Leicester.

(Communicated by R. Whiddington, F.R.S.—Received August 17, 1931.)

When the Raman effect was first discovered, it was believed that every line in the Raman spectrum referred to some characteristic vibration of the scattering molecule. Later the tendency was to regard the lines as due to transitions between states of vibration of the molecule, so that the energies corresponded not to energies of vibration directly, but to differences in the energy of vibration of two different modes. It is now realised that the infra-red spectrum of a substance and the Raman spectrum which it scatters give complementary information. Certain modes of vibration are represented solely in the infra-red spectrum, others are found only in the Raman spectrum, while others may appear in both spectra. Quite early a rough criterion on the basis of symmetry was put forward by Schaefer,* for the determination of whether or not a particular vibration was to be expected in the Raman effect. Recently a selection rule has been formulated by Placzek†; no vibration will appear as a fundamental in the Raman effect if it is such that any symmetrical operation upon it can change the signs of the displacements of the normal co-ordinates, without altering the energy.

It is clear that a knowledge of the normal modes of vibration of the molecule under discussion must precede the application of any such rule, and it is the purpose of the present communication to discuss the normal modes of vibration of the carbonate and nitrate ions. In 1929 the writer showed that it was possible to obtain Raman spectra from powdered crystals, and the discovery was made when using powdered crystals of potassium nitrate. The method was applied first to carbonates and nitrates, so it became of interest to attempt to fix the structure of the anions of these salts by means of the Raman spectra combined with the infra-red data. In what follows the carbonate ion will first be dealt with in some detail, and then the nitrate ion can be treated summarily owing to the similarity of structure of the two ions.

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* 'Der Raman Effekt,' Berlin, p. 12 (1930).

† 'Z. Physik,' vol. 70, p. 84 (1931).

Triangular Structure of the Carbonate Ion.

The crystal structure of calcite has been investigated with X-rays by W. L. Bragg,* W. H. Bragg,† Wyckoff,‡ and others. The three oxygen atoms and the carbon atom lie in a plane, and form an equilateral triangle with the carbon atom at the centre. The optic axis of the crystal is perpendicular to the plane of the triangle.

The vibrations of such a system of four particles have been investigated previously by Brester§ from considerations of symmetry, by Kornfeld|| treating the atoms as charged masses at given distances apart, and by Nielsen¶ who used the elegant method of Dennison. It was when the writer wished to use Nielsen's equations to co-ordinate the nitrate data that he realised that these equations could not be correct, for as printed they are not in their simplest form, neither are they consistent with the characteristic equation earlier in the paper. In consequence, Dennison's** method was employed to calculate the modes of vibration, and a characteristic equation was obtained differing from Nielsen's. It will be shown that the frequency formulæ here put forward are probably correct.

Theoretical Treatment of the Carbonate Ion.

In Dennison's method of treatment, it is assumed that central forces may be employed. Each atom is treated as a centre of force, and it is hoped that polarisations will not seriously upset the character of the normal modes. It is obvious that the conclusions drawn will only be approximations on account of this assumption, but it is believed that *some* of the vibrations will be little affected to a first approximation, while others are more greatly affected. This point will be discussed in the application of the formulæ to the actual cases. In the second place, the amplitudes of vibration of the atoms are to be regarded as small, so that in the evaluation of the kinetic and potential energies powers of the displacements above the second may be neglected.

The CO_3 ion consists of four particles, and has therefore 12 degrees of freedom. Of these we may disregard three by considering only displacements such that the centre of gravity of the ion remains fixed, and three more by adding in the

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* 'Proc. Roy. Soc.,' A, vol. 89, p. 468 (1914).

† 'Phil. Trans.,' A, vol. 215, p. 253 (1915).

‡ 'Amer. J. Sci.,' vol. 50, p. 317 (1920).

§ "Diss.," Utrecht (1923).

|| 'Z. Physik,' vol. 26, p. 205 (1924).

¶ 'Phys. Rev.,' vol. 32, p. 773 (1928).

** 'Astrophys. J.,' vol. 62, p. 84 (1925); 'Phil. Mag.,' vol. 1, p. 195 (1926).

constraint that rotation of the ion as a whole is to be prevented. Thus we are left with six, requiring six co-ordinates to fix the configuration. These are chosen as q_1, q_2, q_3, mutual displacements of the O atoms in pairs, and x, y, z, the components of the displacement, with respect to the centre of gravity of the three O atoms, of the C atom along three mutually perpendicular axes. The x and y axes are in the plane of the triangle, being parallel and perpendicular to one of the sides respectively, and the z axis is perpendicular to the plane of the atoms. (These were the co-ordinates adopted by Nielsen.) With a view to checking errors, the whole calculation was repeated using fixed instead of moving axes for the C atom.

It is easily evident by inspection that the moving co-ordinate z is a normal co-ordinate, and can easily be suppressed by confining displacements to the plane of the triangle, thus leaving only five co-ordinates to be dealt with.

The length of the side of the triangle in its undisplaced state is written a and the normal distance of the C from the O atoms is written r. The forces between the atoms are ascribed to unknown potential functions F and f between the C and the O atoms and between the O atoms in pairs respectively. $F(r)$ and $f(a)$ are then written for the values of these potential functions when the displacements are vanishingly small. If q_4, q_5, q_6 are the relative displacements of the C and the O atoms, then the potential energy for any small displacement is

$$\begin{aligned} V = F(r) + f(a) + F'(r)(q_4 + q_5 + q_6) + \tfrac{1}{2}F''(r)(q_4^2 + q_5^2 + q_6^2) \\ + f'(a)(q_1 + q_2 + q_3) + \tfrac{1}{2}f''(a)(q_1^2 + q_2^2 + q_3^2). \end{aligned}$$

By a consideration of a radial displacement of the O atoms with the C atom at rest, it is easily found that for equilibrium

$$F'(r) + \sqrt{3}\, f'(a) = 0.$$

The potential and kinetic energies are then dealt with separately, being written down as quadratic functions of the co-ordinates and their time derivatives respectively, with arbitrary coefficients. Small displacements are then considered, such that there is no translation of the centre of gravity and no rotation of the ion as a whole, and the coefficients thus evaluated. In the present instance this gave

$$\text{K.E.} = \frac{m}{2}\left\{\frac{3}{\mu}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \tfrac{5}{9}(\dot{q}_1^2 + \dot{q}_2^2 + \dot{q}_3^2) - \tfrac{2}{9}(\dot{q}_1\dot{q}_2 + \dot{q}_2\dot{q}_3 + \dot{q}_3\dot{q}_1)\right\}$$

and

$$\begin{aligned} \text{P.E.} = F(r) + f(a) + \frac{K}{2}\Big\{\tfrac{3}{2}(1 + \beta)(x^2 + y^2) + 3\beta z^2 + \tfrac{1}{3}(1 + 3\alpha)(q_1^2 + q_2^2 + q_3^2) \\ + (1 - \beta)\left[(q_1 - q_2)x + \frac{y}{\sqrt{3}}(2q_1 - q_2 - q_3)\right]\Big\}, \end{aligned}$$

where m is the mass of an O atom and M that of a C atom, and μ is written for $(M + 3m)/M$. K is $F''(r)$, α is $f''(a)/F''(r)$ and β is $F'(r)/r \,.\, F''(r)$. Thus K relates to the C — O binding, α to the ratio of the O — O binding to the C — O binding, and β involves a tension in the equilibrium condition.

The energies are then treated in the ordinary way to obtain the following characteristic determinant :—

$$(\lambda - \beta\mu)\{\lambda - (1 + 3\alpha)\}\{4\lambda^2 - 2\lambda\,[\mu\,(1 + \beta) + (1 + 3\alpha)] \\ + (1 + 3\alpha)(1 + \beta)\,\mu - (1 - \beta^2)\,\mu\}^2 = 0,$$

where $\lambda = 4\pi^2\nu^2 m/\kappa$.

It will be seen that the symmetry leads to degeneracy, since four of the six expected frequencies are replaced by two double frequencies, the remaining two frequencies being single. The four frequencies are

$$\nu_1 = \frac{1}{2\pi}\sqrt{\frac{K}{m}}\sqrt{\eta\mu},$$

$$\nu_{2,3} = \frac{1}{2\pi}\sqrt{\frac{K}{m}}\sqrt{\tfrac{1}{4}[\mu\,(1+\beta) + (1+3\alpha)] \pm\sqrt{[\tfrac{1}{4}\mu(1+\beta) + \tfrac{1}{4}(1+3\alpha)]^2 - \tfrac{1}{4}\mu[(1+3\alpha)(1+\beta) - (1-\beta)^2]}},$$

$$\nu_4 = \frac{1}{2\pi}\sqrt{\frac{K}{m}}\sqrt{(1 + 3\alpha)}.$$

The first and fourth frequencies are the same as were obtained by Nielsen, the middle two are different.

The Normal Modes of Vibration.

In the first frequency, the normal co-ordinate is z, and the carbon atom vibrates perpendicularly to the plane of the triangle, while at the same time the three oxygen atoms move simultaneously in the opposite direction perpendicularly to the plane of the triangle so as to keep the centre of gravity at rest.

In the fourth mode of vibration, the three oxygen atoms simultaneously approach and recede from the carbon atom which remains at rest, the motion being in the plane of the triangle. Thus, the first frequency involves a variation of electric moment and will appear as a fundamental in the infra-red spectrum, while the fourth frequency involves no electric moment and so cannot appear in the infra-red spectrum. On the other hand, a symmetry operation (rotation of the plane of the triangle about an axis in its plane through 180 degrees) does reverse the signs of the displacements without altering the amount of the energy, so that this first frequency cannot appear in the Raman effect as a *fundamental* while the fourth frequency is not so forbidden.

The second and third modes of vibration are considerably more complicated. They can each be represented by the vector sum of two simultaneous modes of vibration. In one, all the oxygen atoms simultaneously move a distance t, say, in a direction perpendicular to one of the sides of the triangle, while the carbon atom moves in the opposite direction a distance $3mt/M$. In the other motion, which is to be superimposed on the first, the oxygen atom centrally placed in the first motion moves a further distance s, say, while the other two oxygen atoms move symmetrically outwards through the same distance s in directions perpendicular to the sides of the triangle (see fig. 1). The ratio of the two displacements are given by:

$$\left(\frac{t}{s}\right)_{2,3} = \frac{2\lambda_{2,3} - (1 + 3\alpha)}{\mu(1 - \beta)},$$

and the angles $\phi_{2,3}$ by

$$\cot\phi_{2,3} = \frac{2}{\sqrt{3}}\left[\frac{2\lambda_{2,3} - (1 + 3\alpha)}{\mu(1 - \beta)} - \tfrac{1}{2}\right].$$

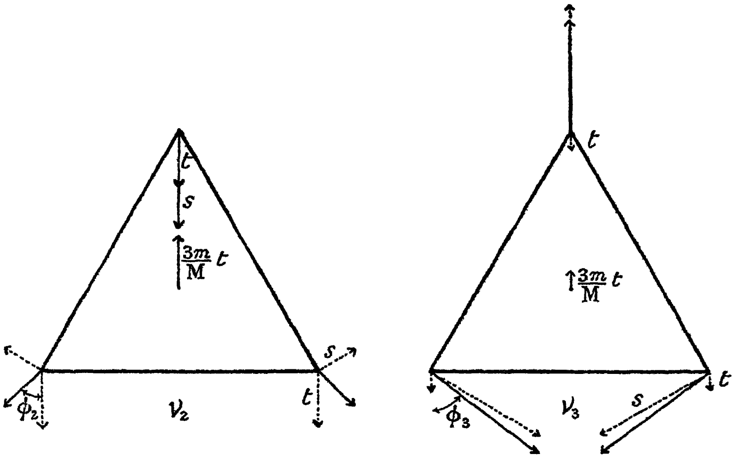


Fig. 1.—Firm lines represent resultant displacements. (The displacements are approximately to scale except that the central atom should move four times as far.)

It is to be remembered, however, that ν_2 and ν_3 are double vibrations. In consequence, to obtain a representation of the actual vibration, we must consider the motion just described, with, say, oxygen atom A as the symmetrically placed one, to be superposed upon the same motion with *either* oxygen atom B *or* C as the symmetrically placed one. Thus the actual motion of an atom will be a kind of elliptical vibration.

Intensities in the Infra-red.

From the modes of vibration, it is possible to deduce the relative intensities which are to be expected in the infra-red. The intensities will depend upon the variations in electric moment, upon the reduced mass of the harmonic oscillator to which the vibration is equivalent, and upon whether the root is single or multiple.

In ν_4, no variation in the electric moment is produced by the motion, consequently this frequency will have zero intensity.

In ν_1, we have a harmonic oscillator of mass $3Mm/(3m + M)$ which vibrates in a direction perpendicular to the plane of the figure, with corresponding variation in electric moment.

In ν_2 and ν_3, although there are two motions superposed in each, only one motion contributes to the change in electric moment, and is equivalent to a harmonic oscillator having the same reduced mass as in ν_1, the motion now being in the plane of the figure with appropriate variation in electric moment. In comparing ν_1 with ν_2 and ν_3, there will be twice the weight to be given to the latter frequencies, since they correspond to double roots, and ν_1 to a single root. In comparing ν_2 with ν_3, it is clear from fig. 1 that the variation in electric moment in ν_2 will be greater than in ν_3, so that ν_2 will be more intense than ν_3.

Confirmation of the Present Solution.

An attempt was made to check the correctness of the solution given above by comparison with the solution given by Dennison for the pyramid on a triangular base, by setting the height of the pyramid equal to zero, and setting β in the present case equal to zero also. The three pyramid frequencies thus obtained are in agreement with the second, third and fourth frequencies in both my solution and Nielsen's and thus no criterion is afforded; the fourth pyramid frequency vanishes.

Next, Kornfeld's solution was examined. In this he assumes that the atoms are ionised, so that the carbon atom possesses a charge Ze (afterwards put equal to $4e$), while each of the oxygen atoms has a charge $-2e$, and that there are polarisation forces. The solution is first worked out with unknown potential functions, and the particular solution is then derived assuming definite laws of attraction and repulsion. It was possible to determine the transformations necessary to derive frequencies from Kornfeld's general solution in terms of the present notation. They are (Kornfeld's symbols on left):—

$$\alpha = 0, \quad Q_1 r^2 = K(1 - \beta) \quad \text{and} \quad 9Q_5 r^2 = K(\beta + 3\alpha).$$

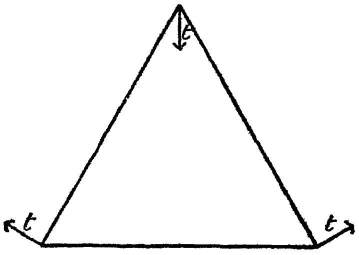
The frequencies deduced from Kornfeld's solution using these transformations are identical with those obtained above.

Further, the normal modes of other simple structures were examined to see if the complicated modes of vibration involved in ν_2 and ν_3 were analogous to modes in these other structures. Such analogous modes were found. The frequency formulæ in the instances given have been worked out also by others, but as the precise modes of vibration have not been determined, they will be given here.

(1) *Equilateral Triangle with Three Atoms.*—This case has been examined by Bhagavantam.* Three equal masses m are situated at the corners of an equilateral triangle, and the second derivative of the potential function is written k. There are three frequencies to be expected, but one is a double one. They are

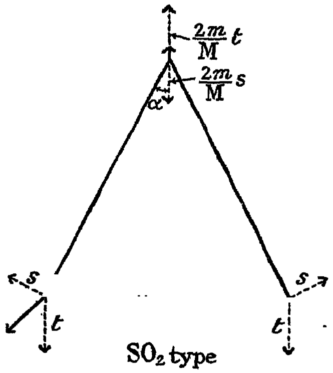
$$\nu_1 = \frac{1}{2\pi}\sqrt{\frac{3k}{m}} \text{ (single)}\dagger \quad \text{and} \quad \nu_2 = \frac{1}{2\pi}\sqrt{\frac{3k}{2m}} \text{ (double)}.$$

The single root refers to the symmetrical "breathing" frequency, while I find the double root is due to one atom moving towards the opposite side, while the other two (fig. 2A) move an equal distance symmetrically outwards perpendicular to the sides—exactly similar to one of the two superimposed vibrations in the case of the CO_3 ion.



O type

FIG. 2A.



SO_2 type

FIG. 2B.

(2) *Isosceles Triangle with Three Atoms.*—This is the case of molecules of the type of SO_2 which has been investigated theoretically by Dennison, and

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* 'Ind. J. Sci.,' vol. 5, p. 73 (1930).

† Bhagavantam gives the double root as ν_1, and the single root as ν_2.

experimentally in the infra-red by Bailey, Cassie and Angus.* The three frequencies are all present as single roots, and have the formulæ

$$\nu_1 = \frac{1}{2\pi}\sqrt{\frac{K}{m}}\sqrt{\left(1+\frac{2m}{M}\sin^2\alpha\right)}$$

and

$$\nu_{2,3} = \frac{1}{2\pi}\sqrt{\frac{K}{m}}\sqrt{\left(\beta+\tfrac{1}{2}+\frac{m}{M}\cos^2\alpha\right)\pm\sqrt{\left(\beta+\tfrac{1}{2}+\frac{m}{M}\cos^2\alpha\right)^2-2\mu\beta\cos^2\alpha}}.$$

The first is a skew vibration which is not of interest in the present connection, but the second and third modes of vibration I find to be a superposition of two simple modes analogous to the two in the CO_3 case. The two m atoms at the base of the triangle move down a distance t, say, while the M atom at the top moves up a distance $\frac{2m}{M}t$. At the same time the two m's move symmetrically outwards perpendicularly to the sides a distance s, say, while the M moves down a distance $\frac{2m}{M} . s . \sin\alpha$ (see fig. 2B). This accounts for one frequency. The other will be similar, but with the displacements t and s so related that M moves $\frac{2m}{M}(t+s)$ while the m's come in. In the above formulæ, β is the ratio of the $m-m$ to the $M-m$ binding, while α is the half-angle at the apex of the triangle. K is the second derivative of the $M-m$ potential function, and consequently relates to the $M-m$ binding.

It will be clear from these two cases that the modes of vibration of the $\nu_{2,3}$ frequencies in CO_3 are reasonable ones. Further, the requirements of degeneracy are satisfied, since the two superposed simple vibrations in CO_3 are each double, so that the sum also will be double.

Application of the Formulæ to Carbonates.

The carbonates have been examined for infra-red spectra by many workers, and in particular by Schaefer† and his co-workers. Three fundamental frequencies are observed, which in the case of calcite are 1430, 880 and 706 (all in cm.$^{-1}$). 1430 is easily the most intense. Further, it has been shown by reflecting polarised light from the surface of calcite crystals that 1430 and 706 belong to the ordinary ray, while 880 is stimulated by the extraordinary ray. Thus 880 must be ν_1 and the other two frequencies must be ν_2 and ν_3. Since it is the larger, 1430 must be ν_2. If the mode of vibration for ν_2 is compared with that for ν_3, for equal kinetic energy of vibration it will be clear that ν_2 will have the larger variation in electric moment and will therefore be the stronger of the two in the infra-red spectrum, which is actually the case. (For equal kinetic energy, t_2 is about three times t_3 and so the intensity of ν_2 will be roughly nine times that of ν_3.)

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* 'Proc. Roy. Soc.,' A, vol. 130, p. 133 (1930).

† "Das Ultrarote Spektrum," Berlin, 1930.

Calcite has been examined for Raman scattering by a number of workers, with the following results :—

*Cabannes	157	221	283	713	1083	1433	1750
Nisi	155	—	282	710	1084	1436	1743
Wood	147–161	—	280	—	1087	—	1730
Schaefer	154	—	281	715	1088	1437	1739
Bhagavantam	159	242	283	717	1087	1440	—

(In all cases to the nearest whole number in cm.$^{-1}$ for ease in comparison.)

715 and 1440 appear, as would be expected, for ν_2 and ν_3. 1087, which is by far the strongest line, is, of course, ν_4. 1739 has been classed by Schaefer, Matossi and Aderhold as $715 + 1087$. I prefer to regard it as $2\nu_1$. It is true that ν_1 itself does not appear in the Raman spectrum, but the selection rule only forbids its appearance as a fundamental—it can well appear in the Raman spectrum as the first overtone. In that case *all four* frequencies can be deduced from the Raman spectrum alone.

The other three frequencies are usually regarded as external (lattice) frequencies. It is not impossible that the smallest one might be a difference $(\nu_1 - \nu_3)$, for such differences may easily occur in the Raman spectrum, and taking Schaefer's numbers the agreement is exact $(\frac{1}{2}\,1739 - 715 = 154)$.

In order to test the fit to the equations, 865, 1440 and 1087 were taken as ν_1, ν_2 and ν_4 respectively, and ν_3 calculated. This gave

$$\beta = 0\cdot2462, \qquad \alpha = 0\cdot315 \quad \text{and} \quad \nu_3 = 644 \text{ (obsd. 715)}.$$

The agreement is at first sight poor, but it must be remembered that the CO_3 ion is embedded in a crystal lattice, and the vibrations of the atoms are bound to be affected.

The values of α and β lead to values of $t/s = 1\cdot317$ and $-0\cdot152$, which makes $\phi_2 = 47\frac{1}{2}°$ and $\phi_3 = -53°$.

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* Cabannes, 'Trans. Faraday Soc.,' vol. 25, p. 813 (1929); Nisi, 'Proc. Imp. Acad. Tokio,' vol. 5, p. 127 (1929); Wood, 'Phil. Mag.,' vol. 6, p. 729 (1928); Schaefer, 'Z. Physik,' vol. 65, p. 289 (1930); Bhagavantam, 'Z. Krist.,' vol. 77, p. 43 (1931).

To see whether the value of K, the C — O binding, is reasonable, we may calculate from the frequencies the value of

$$\frac{1}{2\pi}\sqrt{\frac{K}{m}},$$

and compare it with the values for the same quantity deduced from the band-spectra of CO, making allowance for the different mass. (This method of checking the binding force was suggested to me by the work of Snow.* He, however, underestimates the effect of the alteration of mass from compound to compound.) The vibration frequencies from the infra-red and ultra-violet band spectra of CO in cm.$^{-1}$, are 2155, 1724 and 1104, for the normal state and for the first and second excited states, respectively. Correcting these for mass, they give for the root quantity 1411, 1129 and 723 respectively. From the CO_3 calculations the same quantity is 780, so that it is of the right order and at the same time suggests that the C — O binding in CO_3 is between the second and first excited states and nearer to the former. This also fits in with the chemical evidence.

Aragonite and Calcite.—In the light of the equations obtained for the theoretical frequencies it is interesting to examine the Raman effect measurements of Bhagavantam† recently upon aragonite, since the kation is the same in both crystals, and therefore one source of disturbance is the same. He finds that the frequencies corresponding to ν_4 are the same in both crystals, while ν_3 is smaller in aragonite than in calcite. Aragonite has been examined in the infra-red by Rawlins‡ and Rideal, and they find slight differences between the corresponding frequencies in the two minerals. Comparison is made more difficult by reason of the doubling of the maxima in the transmission curves. Such doubling is to be expected in the cases of ν_2 and ν_3 (since they occur as double roots in the characteristic determinant), if anything occurs to upset the symmetry of the equilateral triangle arrangment of the atoms. Arguing from the point of view of the polarisations of the Raman lines of calcite, Matossi§ concludes that the triangle of O atoms in calcite is slightly isosceles. ν_1 and ν_4, however, should be single, and the values in the two crystals can be directly compared. Schaefer and Matossi (' Das Ultrarote Spektrum,' p. 340) give the following values for ν_1 in the two crystals in cm.$^{-1}$:—

Calcite, 878·7 ; Aragonite, 865·9.

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* ' Proc. Roy. Soc.,' A, vol. 128, p. 294 (1930).

† *Loc. cit.*

‡ See *e.g.*, " Infra-red Spectra," Rawlins and Taylor.

§ ' Z. Physik,' vol. 64, p. 34 (1930).

P. P. Ewald is quoted by Bhagavantam as finding by X-rays a small increase in the C — O distance on passing from calcite to aragonite (1·29 and 1·32 Å. respectively). Unless we know the potentials it is impossible to calculate exactly the effect such a change will have on the frequency. However, by the use of simplifying assumptions we can come to the conclusion that the change in frequency is at any rate in the right direction.

If the forces do not change appreciably in passing from calcite to aragonite, we can take $F'(r)$, $F''(r)$, $f'(a)$ and $f''(a)$ as unchanged to a first approximation, so that κ and α will be practically unaltered. But β is $F'(r)/r \, . \, F''(r)$, and so will vary inversely as the value of r, so that with increasing r, β will decrease. ν_1 is proportional to $\sqrt{\beta}$ so we should have

$$\left(\frac{\nu_{1A}}{\nu_{1C}}\right)^2 = \frac{r_C}{r_A}.$$

Taking the infra-red values,

$$\left(\frac{\nu_{1A}}{\nu_{1C}}\right)^2 = 0 \cdot 971, \quad \text{while} \quad \frac{r_C}{r_A} = 0 \cdot 979.$$

On the other hand, ν_4 which does not contain β should be practically unchanged, and this is the case. When the same calculation is applied to ν_3, however, the alteration in the frequency due to the larger C — O distance is in the right direction, but about four times smaller than the measurements of Bhagavantam show it to be.

Nitrates.—The NO_3 ion is also probably a plane triangular structure and polarisation observations in the infra-red show that the frequency 835 cm.$^{-1}$ belongs to the extraordinary ray, and 727 and 1390 to the ordinary ray. The writer has measured the Raman spectra of many nitrates in the form of crystal powders, and the method has been excellently developed by P. Krishnamurti* in particular and applied by him to nitrates also, but the single large crystal gives clearer spectrograms, so that for the purpose of this calculation the measurements of Schaefer, Matossi and Aderhold† on a single crystal of sodium nitrate will be adopted.

Their numbers are 95, 185, 727, 1070, 1389 and 1669 cm.$^{-1}$.

The last four they identify as ν_3, ν_4, ν_2 and $(\nu_4 + \nu_3)$ respectively. As in CO_3, I prefer to regard 1669 as $2\nu_1$. Similarly it is possible, as in CO_3, that the lowest number is not a lattice frequency, but a difference $(\nu_1 - \nu_3)$. As before, taking the values of ν_1, ν_2 and ν_4, we calculate α, β and ν_3. Their values are

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* 'Ind. J. Phys.,' vol. 5, p. 1 (1930).

† 'Z. Physik,' vol. 65, p. 289 (1930).

0·2717, 0·2493 and 634 respectively. Again, the agreement with the observed (727) is not good, but it is to be remembered that all the effects of perturbing forces are by the method of calculation piled up in the calculated frequency. A better show of agreement would doubtless be made by making a best fit to all four frequencies by the method of least squares, or by the graphical method employed by Trumpy.* But it is doubtful whether all four frequencies should have the same weight attached to them in making such a fit. From the mode of vibration it seems plausible that ν_3 will be the most out. For that reason the procedure already described has been adopted.

Using the calculated values of α and β, $(t/s)_{2,3}$ are found to be 1·293 and $-0\cdot175$, which give $\phi_2 = 47\frac{1}{2}^\circ$ and $\phi_3 = -52^\circ$, which are practically identical with the angles in CO_3.

The values of

$$\frac{1}{2\pi}\sqrt{\frac{K}{m}}$$

calculated from the band-spectra of NO are (normal) 1292, (first excited state) 1602, and (second excited state) 704. The value for the same quantity taken from the calculated frequencies is 794. Thus, as in CO_3, the binding between the N and the O atoms is nearer to that of the second excited state of the NO molecule, which was not anticipated.

Summary.

(1) The frequencies of the normal modes of vibration of the CO_3 and NO_3 ions are calculated, using Dennison's method. Two of the four frequencies are different from those calculated by Nielsen.

(2) Transformations are found which convert Kornfeld's determination of the frequencies into the present notation and agreement is obtained.

(3) The precise mode of vibration is examined and it is found that analogous modes occur in the two most similar structures (O_3 and SO_2).

(4) Infra-red and Raman effect data are used to calculate the constants in the formulæ for the cases of calcite and sodium nitrate. High frequencies in the Raman spectra of each salt are identified as $2\nu_1$, while ν_1 does not occur in the Raman spectra as a fundamental.

(5) The magnitude of the binding forces between the central and the outer atoms suggests, by comparison with band-spectrum data, that they are appropriate to the second excited state of CO and NO respectively.

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* 'Z. Physik,' vol. 66, p. 790 (1930).

I am indebted to Professor Dennison for helpful criticism, and also to Dr. C. P. Snow and Mr. E. V. Whitfield for the benefit of their knowledge of certain points. Some checking of calculations was done by Mr. C. O. Pringle, who is receiving a grant from the Department of Scientific and Industrial Research, to whom I would like to take this opportunity of expressing my thanks.

The Theory of Electronic Semi-Conductors.—II.

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Introduction.

In a previous paper* it was shown that the quantum theory of conduction leads naturally to a division of crystals into conductors and insulators, and various properties of insulators were worked out. Since that paper was written, experimental material has come to my notice which necessitates an extension of the theory to include the effect of impurities, as it appears that impurities dominate the electrical properties of the semi-conductors. As the substances which show a negative temperature coefficient of the electrical resistance fall into two main classes, it will be as well to define what we mean by an electronic semi-conductor. In the first place, there are substances such as silicon which show a negative temperature coefficient in the impure state, but which are good metallic conductors in the pure state and are therefore to be classed as metals. The negative temperature coefficient is probably due to surface effects caused by the presence of oxide, and a tentative theory in this direction has been recently proposed by Frenkel.† Secondly, there are substances such as cuprous oxide which always show a negative temperature coefficient and which become much worse conductors when the amount of impurity present is reduced. Only these latter substances are to be regarded as semi-conductors, and it is with them that we shall deal in this paper. Lastly, there are some substances such as germanium which probably belong to both classes. That is, in some modifications they are metallic and in others insulating.

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* 'Proc. Roy. Soc.,' A, vol. 133, p. 458 (1931), referred to as *loc. cit.*

† 'Phys. Rev.,' vol. 36, p. 1604 (1930).

The treatment of semi-conductors given in the previous paper depends on the fact that the energy spectrum of an electron moving in a perfect lattice splits up into bands of allowed and disallowed energies, and if there are just sufficient electrons present to fill up one of the allowed bands there can be no conductivity at absolute zero temperature. Under these conditions it was shown that if ΔW is the minimum energy required to remove an electron into the next higher band of allowed energies, then for low temperatures the conductivity σ is given by $\sigma = \sigma_0 \exp(-\Delta W/2kT)$. The experimental results* on cuprous oxide can be expressed by such a formula with $\frac{1}{2}\Delta W = 0 \cdot 3$ volt approximately. On the other hand, the inner photo-electric absorption in cuprous oxide† shows that for the pure substance ΔW is about 2 volts, and in general it seems that for all substances ΔW is of the order of a few volts, except for metals where it is, of course, zero. If this is true, then no pure non-metallic solid can ever have a significant natural electronic conductivity at ordinary temperatures, and the observed conductivity of semi-conductors must be due to the presence of impurities. This view is put forward by Gudden and analysed in some detail in the paper quoted above. The evidence seems convincing, and we shall here work out some of the consequences of this hypothesis. Of course, if there should be substances for which ΔW is small, the previous results will apply, but for the substances so far examined ΔW is about 2 volts.

It is easy to obtain a qualitative view of the effect of impurities. Consider first a perfect lattice and a single electron. If the electron is in the neighbourhood of a particular lattice point it can jump to a state of equal energy in the neighbourhood of the next lattice point even although it has to pass through a region where its kinetic energy is negative. In this way an electron can move through the lattice and act as a free electron. This description is correct so long as the lattice is perfect, since the electron can always jump from one state in the neighbourhood of a lattice point to a state of equal energy in the neighbourhood of the next lattice point, as all the lattice points are equivalent. When, however, there are impurities, the case is altered if the electron is originally attached to a foreign atom. For the electron to be free it must be able to jump to a state of equal energy, and this it can only do by jumping to a similar atom, except in the event of the energy level of the foreign atom coinciding with that of the pure substance. Since the transition probability falls off exponentially with distance the probability of an electron jumping from one foreign atom to another is quite negligible if the amount of impurity present is small, and so in general the electrons belonging to impurities are bound electrons and not free. Several cases now arise which may be illustrated by the figure below, which represents a linear lattice in which occurs one foreign atom.

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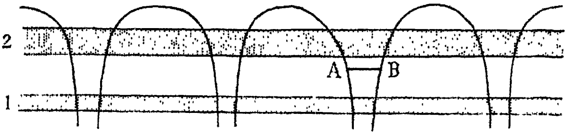
* W. Vogt, 'Ann. Physik,' vol. 7, p. 183 (1930).

† B. Gudden, 'Ber. Phys. Soz. Erlangen,' vol. 62, p. 289 (1931).



The potential energy of an electron is drawn and the shaded bands represent some of the permitted energy bands of the perfect lattice, which are only altered to a negligible degree by the presence of the foreign atom. The foreign atom has a discrete energy level, denoted by the horizontal line AB, which is normally occupied by an electron.

(1) If there are not sufficient electrons per atom of the pure substance to fill up band 1, then the foreign atom will become ionised and its electron will pass over into band 1. In this case the substance is a metal and the only effect of the impurity is to contribute to the residual resistance by acting as a scattering centre for the free electrons.

(2) If there are just sufficient electrons to fill up band 1, then the foreign atom will retain its electron at absolute zero temperature and the whole substance will be non-conducting. At higher temperatures it is possible, owing to the thermal vibrations, for the electron in the state AB to jump to a neighbouring atom of the pure substance. It will then be in band 2 and will be able to act as a free electron. In this case the conductivity will have a factor of the form exp $(-\lambda/kT)$, but λ is not here connected with the minimum energy difference between the bands 1 and 2, but between the state AB and the band 2. It is obviously possible for this latter energy difference to be much smaller than the first, so that the thermal motions can excite electrons from the foreign atoms while quite incapable of exciting those from atoms of the pure substance. It should be noted that electrons on a foreign atom do not take part directly in conduction. They must first be transferred by the effect of the lattice vibrations to an atom of the pure substance. In this case the main function of the impurities is to provide electrons for the upper unoccupied energy bands of the crystal, while acting as scatterers is only a secondary function.

(3) If there are sufficient electrons to fill up band 1 entirely and band 2,

either wholly or in part, then the foreign atom can only act as a scatterer contributing to the residual resistance.

Semi-conductors obviously fall under the second heading and the condition for their occurrence is the presence of impurities such that the minimum energy difference between AB and band 2 is small enough to give a measurable conductivity at ordinary temperatures. If this is the correct view then the occurrence of semi-conductors is purely accidental. This is not in disagreement with the facts as there seem to be no other properties distinguishing insulators from semi-conductors.

The Equilibrium Distribution.

1. The formulæ given in the previous paper have to be modified a little as some of the approximations used no longer hold. The effect of this is to modify the temperature dependence of the conductivity in a way which we shall now work out. We consider as model a simple cubic crystal containing G^3 atoms of which N_0 are foreign atoms. We shall assume that $(G^3 - N_0)/G^3$ is effectively unity, and we shall neglect the disturbing effect of the impurities on the lattice. This latter effect gives rise to a resistance analogous to the residual resistance in metals and could be easily included, as the necessary calculations have been carried out by Nordheim.* This resistance is the dominating factor at very low temperatures, but at ordinary temperatures it is outweighed by the resistance arising from the lattice vibrations, and in order not to complicate the equations too much we shall omit it. We assume that each of the N_0 atoms of impurity possesses a single electron in a discrete state of energy W_1, and that the electrons belonging to atoms of the pure substance form closed shells of energy less than W_1. The next band of allowed energies of the pure crystal is taken to be given by

$$E_{\xi\eta\zeta} = W_2 + 6\beta - 2\beta(\cos\xi + \cos\eta + \cos\zeta), \qquad (1)$$

where the permissible values of ξ, η, ζ are $2\pi G$ $(0, \pm 1, \pm 2, \ldots)$, the notation being the same as in *loc. cit.* We shall only use this expression for small values of ξ, η, ζ, and it then becomes

$$E_{\xi\eta\zeta} = W_2 + \beta(\xi^2 + \eta^2 + \zeta^2). \qquad (2)$$

We suppose that $W_2 > W_1$, and we shall neglect entirely the possibility of any electrons from the closed groups receiving sufficient thermal energy to be excited into these energy levels.

We must first find the distribution of electrons between the various levels when there is thermal equilibrium. The statistics being Fermi statistics, the number of electrons on the foreign atoms is given by

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* 'Ann. Physik,' vol. 9, p. 607 (1931).

$$\frac{N_0}{e^{\frac{W_1-W_0}{kT}}+1}, \tag{3}$$

and the number of electrons with quantum numbers between (ξ, η, ζ) and $(\xi+d\xi, \eta+d\eta, \zeta+d\zeta)$ is given by $(2G^3/8\pi^3)\, n_0\,(\xi\eta\zeta)d\xi\, d\eta\, d\zeta$, where

$$n_0\,(\xi\eta\zeta) = \frac{1}{e^{\frac{E_{\xi\eta\zeta}-W_0}{kT}}+1}, \tag{4}$$

as in *loc. cit.*, section 2. To determine W_0 we have

$$N_0 = \frac{N_0}{e^{\frac{W_1-W_0}{kT}}+1} + \frac{2G^3}{8\pi^3}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\frac{d\xi\, d\eta\, d\zeta}{e^{\frac{E_{\xi\eta\zeta}-W_0}{kT}}+1}, \tag{5}$$

corresponding to *loc. cit.*, equation (25). The work is exactly the same as before, and provided kT is small compared with $(W_2 - W_1)$ and with β, we have

$$W_0 = \frac{W_1+W_2}{2} - \frac{kT}{2}\log\left\{\frac{G^3}{4\pi^3 N_0}\left(\frac{\pi kT}{\beta}\right)^{3/2}\right\}, \tag{6}$$

approximately. To this degree of accuracy (4) becomes

$$n_0\,(\xi\eta\zeta) = \sqrt{\left\{\frac{4\pi^3 N_0}{G^3}\left(\frac{\beta}{\pi kT}\right)^{3/2}\right\}}\, e^{-\frac{W_2-W_1}{2kT}-\frac{\beta\rho^2}{kT}}, \tag{7}$$

where $\rho^2 = \xi^2+\eta^2+\zeta^2$. It is noteworthy that $(W_2 - W_1)/2$ occurs in the exponential factor, and not $(W_2 - W_1)$ as might have been expected. The formula (6) differs from *loc. cit.* (30) by having $(\pi kT/\beta)$ instead of (β_1/β_2). This is because we have taken our lower levels as being sharply defined instead of being spread out into a band, and the approximations previously used do not apply to this case.

The total number of electrons in the upper band is obviously

$$N = \sqrt{\left\{\frac{N_0 G^3}{4\pi^3}\left(\frac{\pi kT}{\beta}\right)^{3/2}\right\}}\, e^{-\frac{W_2-W_1}{2kT}}, \tag{8}$$

and N/G^3 is "the number of free electrons per atom." The meaning of (8) is made clearer if we write it in the following form

$$\frac{N}{G^3} = \frac{(N_0/G^3)^{1/2}}{2\pi^{3/4}}\left(\frac{T}{T_0}\right)^{3/4} e^{-\frac{W_2-W_1}{2kT}}, \tag{9}$$

where $\beta = kT_0$, and N_0/G^3 is the ratio of the number of atoms of impurity present to the number of atoms of the pure substance. This shows that the number of " free electrons " per atom is proportional to $\sqrt{(N_0/G^3)}$, and not to N_0/G^3, which is a very surprising result. Finally

$$n_0(\xi\eta\zeta) = 4\pi^3 \frac{N}{G^3}\left(\frac{\beta}{\pi k T}\right)^{3/2} e^{-\frac{\beta\rho^2}{kT}}, \tag{10}$$

which is equivalent to Maxwell's law.

The Calculation of the Conductivity.

2.1. We must now calculate the change in the distribution function of the free electrons under the combined influence of the lattice vibrations and a constant electric field, F, parallel to the axis of x. We set

$$n(\xi\eta\zeta) = n_0(\xi\eta\zeta) - \xi\chi(E)\, dn_0/dE. \tag{11}$$

In *loc. cit.*, section 3, $\chi(\xi\eta\zeta)$ was used instead of $\xi\chi(E)$, but the latter choice is more convenient here. We then have the following integral equation for χ corresponding to equation (45) *loc. cit.*

$$\frac{2\pi a e F}{h}\frac{dn_0}{dE} = \frac{1}{kT}\sum_{\xi'} A^{+}_{\xi\xi' f}\frac{1}{(e^{\epsilon}+1)(e^{-\epsilon'}+1)(e^{x}-1)}\left\{\chi_{\xi'}\frac{\xi'}{\xi} - \chi_{\xi}\right\}$$
$$+\frac{1}{kT}\sum_{\xi'} A^{-}_{\xi\xi' f}\frac{1}{(e^{-\epsilon}+1)(e^{\epsilon'}+1)(e^{x}-1)}\left\{\chi_{\xi'}\frac{\xi'}{\xi} - \chi_{\xi}\right\}, \tag{12}$$

the notation being the same as in *loc. cit.* except for the difference in meaning of χ. The evaluation of the right-hand side is exactly the same as before and leads to the following result, as may be seen from equation (61) *loc. cit.*

$$\frac{T^3}{\lambda\rho}\int_0^{\frac{\nu h}{\pi a k T}(\rho+\rho_0)} \frac{x^2\,dx}{e^x-1}\left[\chi(\varepsilon+x)\left\{1+\frac{xkT}{2\beta\rho^2} - \left(\frac{\pi a k}{h\nu}\right)^2\frac{2x^2T^2}{\rho^2}\right\} - \chi(\varepsilon)\right]$$
$$+\frac{T^3}{\lambda\rho}\int_0^{\frac{\nu h}{\pi a k T}(\rho-\rho_0)} \frac{x^2\,dx}{e^x-1}\left[\chi(\varepsilon-x)\left\{1-\frac{xkT}{2\beta\rho^2} - \left(\frac{\pi a k}{h\nu}\right)^2\frac{2x^2T^2}{\rho^2}\right\} - \chi(\varepsilon)\right]$$
$$= -F, \tag{13}$$

provided $\rho > \rho_0$, and provided $kT \ll (W_2 - W_1)$ and also $\ll \beta$. The notation is the same as in *loc. cit.* except that

$$\lambda = \frac{ea}{h}\frac{M}{G^3}\frac{16a\beta^2\nu\mu^2}{2\pi C^2}\left(\frac{h\nu}{ak}\right)^3. \tag{14}$$

We have also used the approximation (7) for n_0, which is equivalent to ignoring the effect of the Pauli principle in limiting the transitions to those in which the final states are unoccupied. This is justified since the number of electrons in the upper band is so small that the free electrons are in a non-degenerate state, and obey Maxwellian statistics. When $\rho < \rho_0$ the second integral in (13) disappears, and the bottom limit of the first integral is replaced by

$$(\rho_0 - \rho)\,\nu h/\pi a k\mathrm{T}.$$

The limits of integration take a more familiar form if we introduce the Debye characteristic temperature Θ, defined by

$$\Theta = \frac{\nu h}{ak}\left(\frac{3}{4\pi}\right)^{\frac{1}{3}}.$$

Also

$$\rho_0 = \frac{\nu h}{4\pi a\beta} = \frac{\Theta}{\mathrm{T}_0}\left(\frac{1}{48\pi^2}\right)^{\frac{1}{3}},$$

where $k\mathrm{T}_0 = \beta$. Writing therefore $\kappa = \nu h/(\pi a k\Theta)$, which is a pure number of order unity—equal to $(4/3\pi^2)^{1/3}$ if our model is exact—equation (13) becomes

$$\frac{\mathrm{T}^3}{\lambda\rho}\int_0^{\frac{\kappa\Theta}{\mathrm{T}}\left(\rho+\frac{\kappa\Theta}{4\mathrm{T}_0}\right)}\frac{x^2\,dx}{e^x-1}\left[\chi(\varepsilon+x)\left\{1+\frac{x}{2\rho^2}\left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)-\frac{2}{\kappa^2}\left(\frac{\mathrm{T}}{\Theta}\right)^2\frac{x^2}{\rho^2}\right\}-\chi(\varepsilon)\right]$$
$$+\frac{\mathrm{T}^3}{\lambda\rho}\int_0^{\frac{\kappa\Theta}{\mathrm{T}}\left(\rho-\frac{\kappa\Theta}{4\mathrm{T}_0}\right)}\frac{x^2\,dx}{e^x-1}\left[\chi(\varepsilon+x)\left\{1-\frac{x}{2\rho^2}\left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)-\frac{2}{\kappa^2}\left(\frac{\mathrm{T}}{\Theta}\right)^2\frac{x^2}{\rho^2}\right\}-\chi(\varepsilon)\right]=-\mathrm{F}. \tag{13A}$$

Since the maximum value that x can have is Θ/T, the upper limits must be replaced by this value if $\rho > 1/\kappa$. Such values of ρ, however, play no significant part, and in fact for such large values of ρ the approximations are no longer valid. Now Θ is of order 10^2 degrees, while T_0 is probably of order 10^4, so the most important range of temperatures from a practical point of view, and incidentally the range for which (13A) is most easily soluble, is given by $\Theta < \mathrm{T} < \mathrm{T}_0$. We shall endeavour to obtain a solution assuming that $\Theta \ll \mathrm{T} \ll \mathrm{T}_0$.

We first suppose that $\rho \gg \Theta/\mathrm{T}_0$. Then ε being defined as $\beta\rho^2/k\mathrm{T}$ is $\mathrm{T}_0\rho^2/\mathrm{T}$, while the maximum value of x is $\kappa\Theta\rho/\mathrm{T}$ approximately. Therefore

$$\frac{x}{\varepsilon} = \frac{\kappa}{\rho}\frac{\Theta}{\mathrm{T}_0} \ll 1.$$

It is therefore permissible to expand $\chi(\varepsilon + x)$ as $\chi(\varepsilon) + x\chi'(\varepsilon) + \ldots$. We use this expansion in (13A) and retain only the lowest powers of Θ/T, treating T/T_0 as a small quantity of the same order as Θ/T. The terms of the integrals which are left after these approximations reduce to

$$-\frac{4\mathrm{T}^3}{\lambda\rho}\int_0^{\frac{\kappa\Theta}{\mathrm{T}}\rho}\chi(\varepsilon)\frac{1}{\kappa^2\rho^2}\left(\frac{\mathrm{T}}{\Theta}\right)^2\frac{x^4\,dx}{e^x-1},$$

and so we have

$$\chi = \frac{\lambda F}{\kappa^2 \Theta^2 T} \cdot \frac{1}{\rho}. \tag{14}$$

For values of ρ not large compared with Θ/T_0, I have not been able to solve the equation. It is, however, to be expected that the use of (14) will not introduce a serious error. For values of $\rho < \rho_0$, (13A) becomes

$$\frac{T^3}{\lambda\rho}\int_{\frac{\kappa\Theta}{T}\left(\frac{\kappa\Theta}{4T_0}-\rho\right)}^{\frac{\kappa\Theta}{T}\left(\frac{\kappa\Theta}{4T_0}+\rho\right)} \frac{x^2\,dx}{e^x-1}\left[\chi(\varepsilon+x)\left\{1+\frac{x}{2\rho^2}\frac{T}{T_0}-\frac{2}{\kappa^2}\left(\frac{T}{\Theta}\right)^2\frac{x^2}{\rho^2}\right\}-\chi(\varepsilon)\right]=-F,$$

which can be solved exactly by

$$\chi = \frac{3\lambda F T_0}{2\kappa^3\Theta^3 T}. \tag{14A}$$

It is doubtful how much physical significance is to be attached to this last result, as for such very slow electrons the lattice vibrations can hardly be treated as giving rise to a small perturbation. However, even when we give them their maximum importance, as here, their contribution to the conductivity is quite negligible.

2.2. We must now calculate the current set up by the field, the stream in the x-direction per electron being

$$s_x = \frac{2\pi e a}{h}\frac{\partial E}{\partial \xi} = \frac{4\pi e a \beta}{h}\xi.$$

The total current is therefore

$$J_x = -\frac{4\pi e a \beta}{h}\int \frac{G^3\xi^2}{4\pi^3}\chi(E)\frac{dn_0}{dE}\,d\xi\,d\eta\,d\zeta$$

parallel to the axis of x. For $\rho < \rho_0$, $\chi(E)$ is given by (14A), and for $\rho > \rho_0$ by (14), but since the contribution to the integral from the range $\rho < \rho_0$ is of order $(\Theta^2/TT_0)^2$ compared with the remaining contribution, we may use (14) for the whole range with negligible error. Hence the conductivity σ is given by

$$\sigma = \frac{J_x}{F(Ga)^3} = \frac{16\pi^{1/2}\lambda e \beta^{5/2}(N/G^3)}{3h\kappa^2 a^2\Theta^2 k^{3/2} T^{5/2}}\int_0^\infty \rho^3 e^{-\frac{\beta\rho^2}{kT}}\,d\rho$$

$$= A(N/G^3)\,T^{-3/2} \tag{15}$$

$$= B\,(N_0/G^3)^{1/2}\,T^{-3/4}e^{-\frac{W_2-W_1}{2kT}}, \tag{16}$$

where A and B are complicated constants. Equation (15) gives the variation of σ with the number of free electrons, and equation (16) the variation of σ with the temperature and with the amount of impurity.

We may compare (15) with the classical formula

$$\sigma = \tfrac{4}{3} \frac{e^2 l}{(2\pi mkT)^{\frac{1}{2}}} \frac{N}{(Ga)^3}, \tag{17}$$

where l is the mean free path, and $N/(Ga)^3$ is the number of free electrons per unit volume. This is a purely classical result, and it gives no information about l. The quantum theory shows that l varies as T^{-1} for temperatures above the Debye temperature, and so (17) agrees with (15). In deriving (15) we have made no use of the Fermi distribution, which is only used to determine the variation in the number of free electrons with temperature, and which gives rise to the very surprising result expressed by (16). Formula (15) therefore holds for any semi-conductor, independently of whether the conduction is intrinsic or due to impurities, while (16) is different in the two cases. In fact, if the conduction is intrinsic

$$N \propto T^{3/2} e^{-\frac{\Delta W}{2kT}},$$

and so

$$\sigma = \sigma_0 e^{-\frac{\Delta W}{2kT}}, \tag{16A}$$

where ΔW is the minimum energy difference between the bands 1 and 2.

The Hall Effect.

3. As the Hall effect is very useful in determining the properties of semi-conductors, it is advisable to consider what the theoretical expression for the Hall coefficient should be. Classically the Hall coefficient only depends on the number of free electrons per unit volume and not on the mean free path. We must, therefore, have exactly the classical formula, as the only difference between the classical and quantum treatments of semi-conductors is that the quantum theory makes explicit evaluation of the free path. So the Hall coefficient R is given by

$$R = \frac{3\pi (Ga)^3}{8eN} \tag{18}$$

$$= \frac{3\pi^{7/4} a^{3/2}}{4e} \sqrt{\frac{G^3 a^3}{N_0}} \left(\frac{\beta}{kT}\right)^{3/4} e^{\frac{W_2 - W_1}{2kT}}. \tag{19}$$

We see from (19) that it is not possible to determine directly the number of atoms of impurity present from measurements of the Hall coefficient, as β is not known. However, it is found experimentally that $R\sigma$ is approximately the same for all substances, including semi-conductors, at the same temperature, and as this quantity is mainly determined by β we may assume that for semi-conductors β is of the same order of magnitude as for metals, that is, about 1 volt. It must be admitted that the approximate constancy of $R\sigma$ is not a conclusive proof of the constancy of β, on account of the large number of ill-determined constants occurring in the theoretical formulæ, which are as follows :—

For metals

$$R\sigma = 48\pi^5\kappa^5 \frac{ea^6\nu\beta^2\mu^2}{h^2C^2} \cdot \frac{M}{G^3a^3} \cdot \frac{\Theta}{T}, \tag{20}$$

while for semi-conductors

$$R\sigma = 8\pi^{7/2}\kappa \frac{ea^6\nu\beta^2\mu^2}{h^2C^2} \cdot \frac{M}{G^3a^3} \cdot \left(\frac{\beta}{kT}\right)^{1/2} \frac{\Theta}{T}. \tag{21}$$

The ratio of the numerical factors in the two formulæ is $6\pi^{3/2}\kappa^4$, which is about 2, and if we assume that the other characteristic constants are of the same order of magnitude for metals and semi-conductors, then for $R\sigma$ to be the same in the two cases we must have β^2 for a metal equal to $\beta^2 (\beta/kT)^{\frac{1}{2}}$ for a semi-conductor at ordinary temperatures. This is satisfied if we take β to be about 1 volt in the two cases. Theoretically we should expect β for a semi-conductor to be less than β for a metal, since β measures the " looseness of the binding of the electrons," and as we have no better evidence than the above to go on we shall take 1 volt as being an upper limit for β.

Numerical Results.

4. The only results which seem good enough to be used to test the theory are those of Vogt on cuprous oxide. He finds that the conductivity and the Hall coefficient can be well represented by

$$\sigma = \sigma_0 e^{-q/T} \quad \text{and} \quad R = R_0 e^{q/T}.$$

They can equally well be represented by the formulæ derived here, and the experiments are unable to decide which set is the more correct.

The value of q is about 3900, which corresponds to an energy of about 0·3 volt, and so $(W_2 - W_1)$ is twice this, that is, 0·6 volt. It is a most remarkable feature of the theory that conductivity measurements determine directly $\frac{1}{2}(W_2 - W_1)$, while the inner photoelectric effect determines $(W_2 - W_1)$. Unfortunately, an experimental verification of this point seems to be extremely difficult, since for pure substances for which the photoelectric effect is easily measurable the conductivity is infinitesimal, while for impure substances with a measurable conductivity the amount of impurity present is so small that the corresponding absorption cannot be detected with certainty.

Vogt finds that the Hall coefficient of one specimen can be expressed as

$$eR = 10^{-18}\, e^{3900/T},$$

and concludes that there are 10^{18} atoms of impurity per cubic centimetre. This is not true, since Boltzmann's law does not hold. Using equation (19) we may express R as

$$eR = 10^{-16}\, T^{-3/4}\, e^{3900/T},$$

and so

$$\sqrt{\frac{N_0}{G^3 a^3}} = \tfrac{3}{4}\pi^{7/4}\, a^{3/2}\, 10^{16} \left(\frac{\beta}{k}\right)^{3/4}.$$

Putting $a^3 = 10^{-22}$ c.c. and $\beta = 1$ volt, we obtain for N_0/G^3a^3 about 10^{17}, and so there are about 10^{17} atoms of impurity per cubic centimetre, while there are about 10^{22} molecules of Cu_2O per cubic centimetre. This is a conclusive proof that the conductivity is due to impurities and is not intrinsic.

To sum up, we may say that the experiments do not contradict the theory, but this can hardly be taken as a proof of the correctness of the latter, since the assumptions made by Vogt are also adequate to explain the known facts. However, the advantage of the present theory is that it gives a definite meaning to the idea of a " free electron," and the number of these is not arbitrary but is definitely fixed by the arrangement of the energy levels. The most important point in the theory—the occurrence of $\frac{1}{2}(W_2 - W_1)$ in the expression for the conductivity—does not seem capable of being tested at the moment.

The Measurement of the Viscosity of Gases at High Pressures.—The Viscosity of Nitrogen to 1000 *Atms.*

By A. MICHELS and R. O. GIBSON.

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According to the classical kinetic theory the viscosity of a gas is independent of the density and increases with increasing temperature. The experimental verification of this at ordinary pressures provided "one of the most striking triumphs of the theory."* The viscosity of liquids, however, has been shown to be very sensitive to small changes in density and to decrease with increasing temperature.†

It is thus of interest to measure the viscosity of gases under increasing pressures in order to follow its change as the density becomes comparable with that of liquids. But little experimental work has as yet been done along these lines. Warburg and Von Babo‡ and P. Phillips§ have determined the viscosity of carbon dioxide between 20° and 40° C. up to 120 atmospheres. Wildhagen|| made some measurements with air at room temperature up to 200 atmospheres, and Boyd¶ has worked with nitrogen, hydrogen and their mixtures at 30°, 50° and 70° C., up to 200 atmospheres.

With carbon dioxide the viscosity increases continuously with density to the higher viscosities typical of the liquid state. Below the critical temperature the viscosity-density curves for the liquid and the gaseous states are apparently continuous. The viscosities of the other gases also show a tendency to increase with increasing pressure.

A method is described in the present paper for the measurement of the viscosity of gases at high pressures and the results are given for nitrogen up to 1000 atmospheres. The measurements have not been carried to higher pressures owing to the lack of reliable compressibility data needed in the calculation of the results.

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* Jeans, "The Dynamical Theory of Gases," chap. 11, p. 294 (2nd ed., 1916).

† *Cf.* Hatschek, "The Viscosity of Liquids," chaps. 5 and 6 (1928).

‡ E. Warburg and L. von Babo, 'Wied. Ann.,' vol. 17, p. 390 (1882).

§ P. Phillips, 'Proc. Roy. Soc.,' A, vol. 87, p. 48 (1912).

|| Max Wildhagen, 'Z. Angew. Math. Mechanik,' vol. 3, p. 181 (1923).

¶ J. H. Boyd, 'Phys. Rev.,' vol. 35, p. 1284 (1930).

The Method.

A method based on the transpiration of gas through a narrow capillary was chosen as the most suitable for adaptation to high pressures. Methods involving the damping of oscillations, measurement of torque, etc., would necessitate a knowledge of the change of the elastic constants of the suspensions with pressure before the absolute viscosities could be calculated.

The theory of the transpiration method, which is fully treated in the text-books,* leads to Poisseuille's relationship for a fluid

$$I = -\frac{\pi}{8\eta} r^4 \rho \frac{dp}{dl},$$

where I is the mass of fluid, of density ρ and viscosity η flowing in unit time through a capillary of radius r under a pressure gradient dp/dl.

Before integrating in the case of a gas, where ρ is not constant over the length of the capillary, this expression must be rearranged to give

$$-\frac{\pi}{8\eta} \rho\, dp = I \frac{dl}{r^4}.$$

If it is assumed that η and I are constant over the length of the capillary, then

$$-\frac{\pi}{8\eta} \int_{p_1}^{p_2} \rho\, dp = I \int_0^l \frac{dl}{r^4}.$$

This expression, which may be rewritten

$$I = -\frac{\pi}{8\eta} \frac{\int_{p_1}^{p_2} \rho\, dp}{\int_0^l \frac{dl}{r^4}}, \tag{1}$$

shows what quantities must be considered in designing the apparatus.

According to the theory of Reynolds,† the pressure difference $p_1 - p_2$ to avoid turbulent flow in the capillary must be comparatively small. A preliminary calculation showed that, for nitrogen, with a tube 80 cm. long and with a diameter of the order of 0·1 mm. pressure differences up to about 1 atmosphere could be used.

To obtain an accurate evaluation of $\int_0^l \frac{dl}{r^4}$ it was advisable to use a glass capillary so that the variation of the diameter over the whole length could be measured. The use of a glass capillary necessitated the application of an internal and an external pressure of the same order. This at the same time simplified the calculation of the effect of the pressure on the dimensions of the capillary.

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* *E.g.*, Barr, "A Monograph on Viscometry," chap. 7 (1931).

† Barr, *loc. cit.*, p. 5, etc.

The chief problem in designing the apparatus was to find a means of measuring accurately pressure differences of the order of ½ atmosphere at a high total pressure. In order that the method adopted may be readily understood, a description will be given in terms of the diagrammatic sketch (fig. 1).

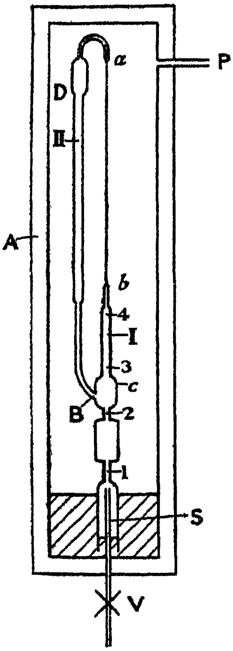

Fig. 1.

The viscometer consists of a glass apparatus with a capillary (*ab*). This is placed in a steel vessel (A) containing mercury at the bottom, the remainder being afterwards filled with oil. The glass apparatus is filled with the gas under investigation through the narrow steel tube (S).

A known pressure is applied to the oil at P causing the mercury to rise inside the glass. The height of the mercury can be indicated at four points (1, 2, 3, 4) where it makes contact with platinum wires sealed through the glass. The total mass of gas in the apparatus is first found from measurements of the pressure at each of the contacts 1 and 2 and from a knowledge of the volume between them, or that of the whole apparatus.

The pressure is then increased. When the mercury passes the glass junction (B) it compresses the gas in the two portions (I and II) independently, so long as the rate of increase of pressure is large compared with the rate of transpiration of the gas through the capillary. Under these conditions the mercury may rise to the positions C and D and, if the pressure is then maintained constant, the gas transpires through the capillary under this head of mercury.

The time taken for the mercury to rise between the contacts 3 and 4 is measured. As the volume between these contacts had been calibrated and the pressure is known, the mass of gas passing through the capillary in a known time is measured. The pressure difference is calculated from a knowledge of the dimensions of I and II, and of the total quantity of gas present in the apparatus. In this connection a knowledge of the compressibility isotherms of the gas is essential.

Any measurement can be repeated by lowering the pressure till the mercury is below the junction B and then increasing it again rapidly. In order to work at higher or lower pressures, the pressure is decreased till the mercury is below the top of the tube (S), when gas can be added to or removed from the apparatus through the valve (V).

The dimensions of the glass work are so chosen that the mercury level in I after the rapid compression is some distance below the first time contact 3, so that there is sufficient time for the heat of compression to be dissipated before the run begins.

The Apparatus.

Dimensions of the Viscometer.—A scale drawing of the viscometer in detail is given in fig. 2. The steel mantle is shown in 2A, the glass work in 2C, and the mounting for it in 2D.

In order to simplify the calculations, it was desirable that the tubes (I *b* and II *b*), in which the mercury rises and falls respectively during the viscosity run, should have as nearly the same diameter as possible. As tubes of 1 sq. cm. area guaranteed uniform better than 1 in 1000 could be obtained from Schott and Genosse of Jena, made of their standard 16 III glass, these were used for the two parts in question. Care was taken in sealing the contacts 3 and 4 to cause as little deformation as possible. In such tubes the correction for the capillary depression of the two mercury surfaces is less than 0·03 cm., so that the pressure difference must be of the order of 30 cm. to ensure an accuracy of 1 in 1000.

In order to obtain the same accuracy in the volume measurements, it was unnecessary for I *b* to have a volume greater than 16 c.c. as the mercury surface rises steadily to both contacts. It was found during the calibration that a reproducibility of at least 1 in 2000 could be obtained for this volume.

The greatest length of capillary that could conveniently be used was 80 cm. As has already been mentioned, the desirable diameter of this tube must be of the order of 0·1 mm., in the case of nitrogen, for the range of pressure differences to be used.

The Calibration.—The following dimensions of the apparatus were measured before assembling:

(1) $\int_0^l \frac{dl}{r^4}$ for the capillary.

(2) The volumes I *b* between the platinum contacts and I *c* between the top contact and the entrance of the capillary.

(3) The volume II from the end of the capillary (*a*) as a function of the distance from a fixed point on II *b*.

(4) The volume between the contacts 1 and 2.

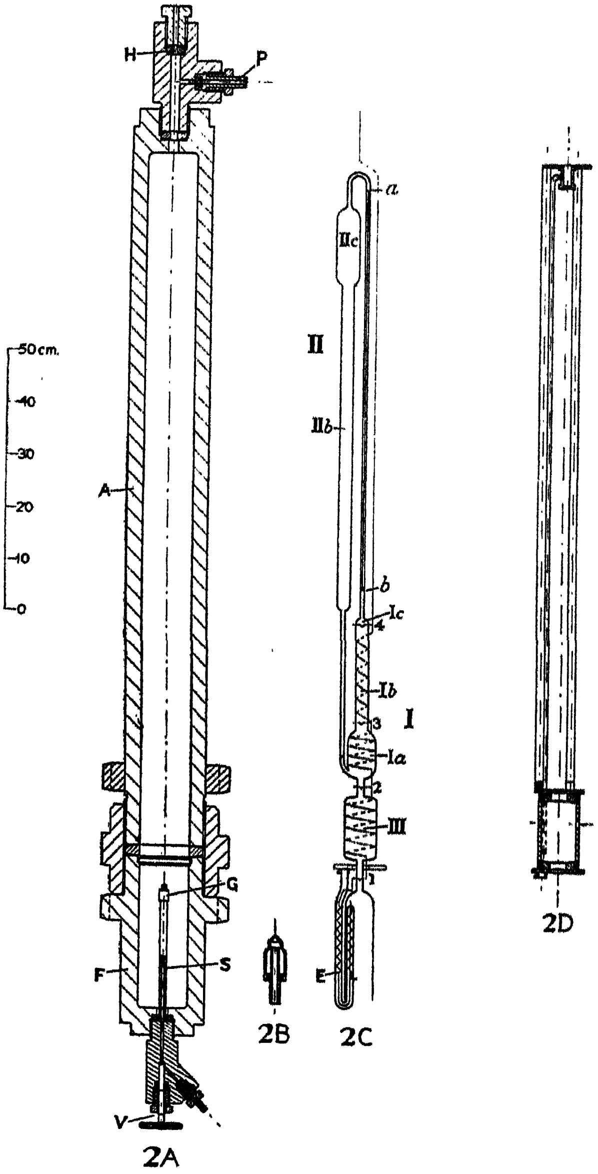

Fig. 2.

(1) A number of capillary tubes of Jena 16 III glass were examined for uniformity and roundness of bore and for freedom from subsidiary capillaries, and one of the required diameter was chosen. The ellipticity was less than 2 per cent., in which case it can be shown that the error in the viscosity by assuming the tube round is less than 0·1 per cent.*

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* Barr, *loc. cit.*, p. 65.

The tube was calibrated by a procedure similar to that described by Schultze* and by Fisher,† although the method of computation was somewhat different. The mean area was determined from the weight of a measured thread of mercury filling the length l of the tube to be used. In this way the mean square of the radius R^2 was obtained, whilst the mean of r^4 is required. The length of a small pellet of mercury was therefore measured in different positions in the tube.

As is shown by Fisher

$$\int_0^l \frac{dl}{r^4} = \frac{\pi^2}{V^2}\left[\int_0^l \lambda^2 \, dl\right]\left[\int_0^l \frac{dl}{\lambda}\right]^2$$

where λ is the length of the pellet and V is the volume of the length l.

Fisher evaluated this expression graphically, but if the lengths of the pellet have been measured end to end along the tube, then substitution of

$$V = \pi R^2 l$$

and

$$\lambda = \lambda_m + \Delta$$

(where λ_m is the mean length of the pellet and Δ is the deviation from it) leads to

$$\frac{l}{R^4}\left\{1 + \frac{1}{\lambda_m{}^2 l}\int_0^l \Delta^2 \, dl\right\}^3.$$

Instead of obtaining the value of the integral $\int_0^l \Delta^2 dl$ graphically, it is possible to replace it by the sum $\Sigma\Delta^2\lambda_m$, assuming that the tube is homogeneous over the length of the small pellet. In this case the expression becomes

$$\frac{l}{R^4}\left(1 + \frac{\Sigma\Delta^2}{\lambda_m l}\right)^3$$

or, on expanding and neglecting all terms of higher order than Δ^2

$$\frac{l}{R^4}\left(1 + 3\frac{\Sigma\Delta^2}{\lambda_m l}\right).$$

In order to be able to use this method, an arrangement was made by which the pellet could be adjusted in any position in the tube.

At the ends, where the capillary widens rapidly, the values of l/r^4 were calculated for overlapping lengths and added to the value of $\int_0^l \frac{dl}{r^4}$ obtained as above to give the final value to be used in equation (1) to calculate the viscosity.

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* H. Schultze, 'Ann. Physik,' vol. 5, p. 140 (1901).

† W. J. Fisher, 'Phys. Rev.,' vol. 28, p. 73 (1909).

(2) For the calibration of the volume I *c*, a length of glass tube, about 2 mm. in diameter, was etched with divisions at every $\frac{1}{2}$ cm. and calibrated by weighing with mercury. Part of this tube was sealed on to the top of I *c* and part to the end of the capillary (*b*).

The volumes between the contacts and from the top contact to the divisions of the narrow tube, were obtained by the method already described by the authors in connection with the calibration of piezometers for isotherm measurements.*

The volume from the divisions to the entrance of the capillary was measured in a similar way. The 2 mm. tubes were joined together amongst the divisions, so that the volume from the top contact to the entrance of the capillary could be calculated, the uncertainty due to the fuse being less than the required accuracy.

(3) The tube II *b* was supplied etched at every centimetre and the cross section of this tube was controlled by weighing with mercury. The volume II *c* from a fixed mark on II *b* to the entrance of the capillary was calibrated by a similar process to I *c*, using a length of 2 mm. tube.

(4) Volume III between the contacts 1 and 2 was obtained by the same method as I *b*.

Further Details of the Apparatus.—Two precautionary details of the apparatus may be particularly mentioned. During the working of the apparatus the mercury was, of course, above the top of the steel tube (S). In this case there was a chance of gas, trapped in the tube and valve, being displaced by mercury when the pressure was raised and so altering the amount present during the measurements. To avoid this a steel hood (G), shown on a larger scale in fig. 2B, was fitted to the top of the tube. The volume of the hood was such that, whatever the position of the mercury, none could enter the tube.

It has already been mentioned that when the apparatus was filled with gas the mercury level must be brought below the top of the tube (S). In order to ensure that the mercury was in the correct position, and not too high or too low, the safety device shown at (E), fig. 2C, was fitted. This consisted of a glass U-tube containing a resistance wire with two platinum points sealed through it in such positions that the mercury level was correct if it lay between them.

All the platinum contacts in the apparatus were linked together with resistances to form one arm of a Wheatstone's bridge in a manner similar to that already described by the authors.* When the mercury reached a contact the bridge was disturbed and the fact indicated by the deflection of a galvanometer.

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* A. Michels and R. O. Gibson, 'Ann. Physik,' vol. 87, p. 850 (1928).

Assembling of the Apparatus.—The first stage was carried out as follows: the lower part of the steel vessel (F) was fitted with the valve (V), the tube (S) and hood (G), and filled with the required amount of mercury. The cleaned and dried glass work fitted with the safety contact tube and mounted in the brass frame (fig. 2D) was then placed in the lower vessel (F).

In order to appreciate the next stage it may be remembered that, as has already been mentioned in the description of the method, during the measurements the pressure was applied at (P). This pressure was measured and kept constant by means of a pressure balance similar to that described by one of the authors.†

The whole system from the piston of the balance to the surface of the mercury was filled with oil, of which the density was known as a function of pressure and temperature. It was therefore possible to calculate the pressure at any point in the oil from a knowledge of the pressure at the balance and the height of the point with reference to the piston. As, however, the pressure on the gas was required, the correction for the mercury head inside the viscometer had to be determined.

For this purpose a wide glass tube was fitted over the viscometer, mounted as described above, and a gas-tight joint made to the vessel (F). Connections were made from the glass tube, and the valve (V) to the two sides of a differential mercury manometer and to vacuum pumps. The inside and outside of the viscometer were then evacuated at the same time. The valve (V) was then shut and air admitted to the outer tube, forcing the mercury up inside the viscometer. When the mercury touched any of the contacts the pressure difference on the manometer was read with a cathetometer. This gave the desired mercury head. The relative heights of the different parts of the apparatus needed in the calculations were measured at the same time with the cathetometer.

The outside tube was then again evacuated until the mercury level inside the viscometer was below the hood (G). The apparatus was filled with nitrogen through the valve (V) until the pressure was about 90 cm. of mercury, air being admitted to the outer tube at the same rate. The outer glass tube was then removed and the steel jacket (A) placed in position. The insulated electrical lead at (H) was fitted and the system filled with oil.

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* *Loc. cit.*

† A. Michels, 'Ann. Physik,' vol. 72, p. 285 (1923); vol. 73, p. 579 (1924).

The completely assembled pressure vessel was placed in a closed thermostat and the connections made to the press. The thermostat was double-walled and in it the temperature could be maintained constant to ±0·001° C. for considerable periods of time.

The temperatures were measured with mercury thermometers divided in 0·01°, which were completely immersed in the thermostat and read by means of a periscopic device. This arrangement avoided the stem correction and made it possible to control the temperature equilibrium between different points in the thermostat.

Experimental Procedure.

With the mercury level between the two safety contacts, pure nitrogen from a cylinder was admitted to the apparatus by the valve V which could be controlled through the bottom of the thermostat. The gas was passed through a copper helix cooled in solid CO_2 and alcohol before entering the apparatus.

The valve V was then shut and pressure applied at P until the mercury reached the first contact where the pressure was measured with the balance. The pressure was increased again and the measurement repeated at the second contact. Sufficient data were thus obtained to calculate the total amount of gas in the apparatus. It may be noted that the volume between the contacts was about half of the total volume and, therefore, that the accuracy of the measurement was only about half that of the available isotherm data.

After the normal volume had been measured, the pressure was rapidly increased to give about the desired pressure difference and then kept constant with the help of the pressure balance whilst the gas transpired through the capillary. After a lapse of 30 to 60 minutes the mercury reached contact 3, causing a Weston galvanometer relay, placed in the Wheatstone's bridge circuit, to start a stop-clock. When the mercury reached contact 4 the same relay stopped the clock. The time was thus measured for the mercury to drive a known amount of gas through the capillary.

The clock could be read to one-fifth second, and, when not in use for measurements, was checked against the time signal broadcast from Nauen. The clock lost about 6 seconds in 24 hours, a correction which could be neglected.

The nitrogen used in these measurements was the purest obtainable from Hoek & Son, of Schiedam. The makers guaranteed it free from oxygen and to contain less than 0·01 per cent. of impurities.

Calculation.

In order to calculate the viscosity from the experimental data by means of the expression

$$\mathrm{I} = -\frac{\pi}{8\eta}\frac{\int_{p_1}^{p_2}\rho\,dp}{\int_0^l \frac{dl}{r^4}} \tag{1}$$

given in the introduction, it is necessary to integrate to give

$$\mathrm{M} = \int_0^{\mathrm{T}} \mathrm{I}\,dt = \int_0^{\mathrm{T}} \frac{\pi}{8\eta}\frac{-\int_{p_1}^{p_2}\rho\,dp}{\int_0^l \frac{dl}{r^4}} \tag{2}$$

where M is the total mass of gas passing through the capillary in time T.

This, however, involves a knowledge of the pressures on the gas in both parts of the apparatus and therefore, also, the densities as a function of time. This function is so far unknown. The total mass of gas M transpiring through the capillary is also difficult to calculate as the pressure in volume (I) varies with time.

As the total pressure is kept constant during a run by means of the pressure balance, the pressure at a given level in the mercury remains constant. Under these conditions the pressure on the gas, and therefore the density on both sides of the apparatus, will be a simple function of the heights of the mercury above this level. The right-hand side of expression (2) may therefore be expressed in terms of these two heights, or in terms of the height of the mercury on one side above a fixed level and the pressure difference (Δp) corresponding to the mercury head. There is a connection between these two variables from the fact that the total quantity of gas in the system remains constant.

In the present calculation the level of contact (4) has been taken as the fixed level and the distance, n, an unknown function of time, measured down from it. Equation (1) then has the form

$$\mathrm{I} = \frac{1}{\eta} f_1(n). \tag{3}$$

Now

$$\mathrm{I} = -\frac{d\mathrm{Q}}{dt} = -\frac{d\mathrm{Q}}{dn}\cdot\frac{dn}{dt}, \tag{4}$$

where Q is the mass of gas in volume (I) which may be expressed as a function of n giving

$$I = f_2\left(n, \frac{dn}{dt}\right). \qquad (5)$$

The elimination of I between (3) and (5) gives

$$f_3\left(n, \frac{dn}{dt}, \eta\right) = 0. \qquad (6)$$

This on integration gives an expression in terms of η, λ and T, from which η may be calculated from the experimental data, λ being the distance between the contacts 3 and 4, and T the total time of flow.

The following relationships between the pressures and volumes which are needed in the calculation may first be written :—

(α) $$p_1 = p + n\kappa,$$

where p_1 is the pressure in the gas in (I) and p the constant pressure in the mercury at the level of contact (4). κ is a factor introduced to change a pressure unit of 1 cm. of mercury into atmospheres.

(β) $$p_2 = p_1 - \Delta p,$$

where p_2 is the pressure in the gas in volume II and Δp the pressure difference corresponding with the mercury head.

(γ) $$V_1 = V_{(Ic)} + an,$$

where V_1 is the volume from the mercury level in (I) to the entrance of the capillary, $V_{(Ic)}$ the volume from the top contact (4) to the entrance of the capillary and a the cross section of the tube (I b).

(δ) $$V_2 = V_{(IIc)} + b\left(H + n - \frac{1}{\kappa}\Delta p\right),$$

where V_2 is the volume above the mercury in (II), $V_{(IIc)}$ the volume from the fixed mark at the top of the tube (II b) to the capillary, H the distance from contact (4) to this mark on (II b) and b the cross section of the tube.

(ϵ) $$\rho = \rho_0 \frac{p}{f(p)},$$

where ρ is the density and $f(p)$ the experimental value of pv of the gas expressed in Amagat units (*i.e.*, p in international atmospheres and v in volumes of gas at 0° C. and 1 atmosphere).

The accuracy of the method is limited by the knowledge of these isotherms as is mentioned on p. 303.

$$(\zeta) \qquad Q = \rho_1 V_1 = \rho_0 \frac{p_1}{f(p_1)} V_1 = \rho_0 \frac{1}{f(p_1)} (p + n\kappa)(V_{(Ic)} + an).$$

It is now possible to substitute in equation (1) and, by using relation (ε) to obtain

$$I = -\frac{\pi}{8\eta} \rho_0 \frac{\int_{p_1}^{p_2} \frac{p\,dp}{f(p)}}{\int_0^l \frac{dl}{r^4}}. \tag{7}$$

If it can be assumed that, within the desired limits of accuracy, $f(p)$ is constant over the pressure range $(p_1 - p_2)$ this may be written

$$I = -\frac{\pi}{8\eta} \frac{\rho_0}{f(p) \int_0^l \frac{dl}{r^4}} \cdot \tfrac{1}{2} (p_2^2 - p_1^2), \tag{8}$$

or, with the help of the results given in the note (p. 300)

$$I = \frac{\pi \rho_0}{16\eta f(p) \int_0^l \frac{dl}{r^4}} \cdot (K + Ln + Mn^2). \tag{3*}$$

Substitution of relation (ζ) in equation (4) gives

$$I = -\frac{\rho_0}{f(p)} (ap + \kappa V_{(Ic)} + 2a\kappa n) \frac{dn}{dt}. \tag{5*}$$

Elimination of I between (3*) and (5*) gives

$$\frac{\pi}{16\eta \int_0^l \frac{dl}{r^4}} \cdot (K + Ln + Mn^2) + (ap + \kappa V_{(Ic)} + 2a\kappa n) \frac{dn}{dt} = 0, \tag{6*}$$

which may be written

$$\frac{\pi}{16\eta \int_0^l \frac{dl}{r^4}}\, dt = -\frac{ap + \kappa V_{(Ic)} + 2a\kappa n}{K + Ln + Mn^2}\, dn. \tag{9}$$

Integration of (9) gives

$$\eta = \frac{\pi}{16 \int_0^l \frac{dl}{r^4}} \quad \frac{T}{\int_0^\lambda \frac{ap + \kappa V_{(Ic)} + 2a\kappa n}{K + Ln + Mn^2}}\, dn \tag{10}$$

which can be evaluated.

Corrections.

The corrections for calculating the pressure from the experimental data of the pressure balance are applied in the manner described in the paper previously quoted.* These include the corrections for the thermal expansion and com-

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* *Loc. cit.*

Note.—The required relationship between Δp and n and therefore the expression of $-(p_2^2 - p_1^2)$ in terms of n for substitution in equation (6) may be obtained in the following way:—

The normal volume, N (*i.e.*, the volume at N.T.P.) of the gas in the apparatus can be expressed as the sum of the normal volumes in the two parts I and II

$$\mathrm{N} = \frac{p_1\mathrm{V}_1}{f(p_1)} + \frac{p_2\mathrm{V}_2}{f(p_2)}.$$

As it is assumed that $f(p_1) = f(p_2)$, then substitution of the expressions α, β, γ and δ for p_1, V_1, p_2 and V_2 gives

$$\mathrm{N}f(p) = (p + \kappa n)(\mathrm{V}_{(\mathrm{I}c)} + an) + (p + \kappa n - \Delta p)\left\{\mathrm{V}_{(\mathrm{II}c)} + \frac{b}{\kappa}(\kappa\mathrm{H} + \kappa n - \Delta p)\right\}$$

or

$$(\kappa n - \Delta p)^2 + \mathrm{A}(\kappa n - \Delta p) + \mathrm{X} + \mathrm{Y}n + \mathrm{Z}n^2 = 0,$$

where

$$\mathrm{X} = \frac{\kappa}{b}[p(\mathrm{V}_{(\mathrm{I}c)} + \mathrm{V}_{(\mathrm{II}c)} + b\mathrm{H}) - \mathrm{N}f(p)],$$

$$\mathrm{Y} = \frac{\kappa}{b}[\kappa\mathrm{V}_{(\mathrm{I}c)} + ap],$$

$$\mathrm{Z} = \kappa^2\frac{a}{b},$$

$$\mathrm{A} = \frac{\kappa}{b}\left[\frac{b}{\kappa}p + \mathrm{V}_{(\mathrm{II}c)} + b\mathrm{H}\right].$$

Solution of the quadratic gives

$$\Delta p - \kappa n = \frac{\mathrm{A}}{2} \pm \tfrac{1}{2}\sqrt{\mathrm{A}^2 - 4(\mathrm{X} + \mathrm{Y}n + \mathrm{Z}n^2)},$$

which may be expressed in a form more adaptable to numerical calculation by first expanding to give

$$\Delta p - \kappa n = \frac{\mathrm{A}}{2} - \tfrac{1}{2}\sqrt{\mathrm{A}^2 - 4\mathrm{X}} + \frac{\mathrm{Y}n + \mathrm{Z}n^2}{\sqrt{\mathrm{A}^2 - 4\mathrm{X}}} + \frac{\mathrm{Y}^2n^2}{(\sqrt{\mathrm{A}^2 - 4\mathrm{X}})^3} + \dots,$$

which on further expansion gives

$$\begin{aligned}\Delta p - \kappa n = {} & \mathrm{A}\left\{\left(\frac{\mathrm{X}}{\mathrm{A}^2}\right) + \left(\frac{\mathrm{X}}{\mathrm{A}^2}\right)^2 + 2\left(\frac{\mathrm{X}}{\mathrm{A}^2}\right)^3 + \dots\right\} \\ & + \frac{\mathrm{Y}}{\mathrm{A}}\left\{1 + 2\left(\frac{\mathrm{X}}{\mathrm{A}^2}\right) + 6\left(\frac{\mathrm{X}}{\mathrm{A}^2}\right)^2 + \dots\right\}n \\ & + \left[\frac{\mathrm{Z}}{\mathrm{A}}\left\{1 + 2\left(\frac{\mathrm{X}}{\mathrm{A}^2}\right) + 6\left(\frac{\mathrm{X}}{\mathrm{A}^2}\right)^2 + \dots\right\} + \frac{\mathrm{Y}^2}{\mathrm{A}^3}\left\{1 + 6\left(\frac{\mathrm{X}}{\mathrm{A}^2}\right) + 30\left(\frac{\mathrm{X}}{\mathrm{A}^2}\right)^2 + \dots\right\}\right]n^2.\end{aligned}$$

Now

$$-(p_2^2 - p_1^2) = \Delta p(2p + 2\kappa n - \Delta p),$$

pressibility of the oil and mercury columns. There are, however, two corrections to which special attention must be drawn.

(1) *Hydrostatic Head of Gas.*—At high pressures the density of the gas is no longer negligible compared with that of mercury. The effective driving force Δp_{eff} on the gas passing through the capillary will be correctly given by an expression which calculation shows to be

$$\Delta p_{eff} = \left(\frac{d - \rho}{d}\right) . \Delta p,$$

where Δp is the head of mercury and ρ and d the densities of the gas and mercury respectively. The density of the gas ρ may be assumed constant throughout the apparatus. Therefore the only correction for gas density is the factor $(d - \rho)/d$ which is constant for any given measurement and can be introduced into equation (8).

(2) *The Hagenback-Couette Corrections.*—It is generally accepted that the slip of the gas along the wall of the capillary can be neglected except for very low pressures. Part of the effective pressure difference, however, is used to accelerate the gas on entering the capillary and along its length on account of the expansion, and, also, to overcome the extra friction in the first part of the capillary before the flow has become laminar.

These corrections, known as the Hagenback and Couette corrections, have recently been discussed by Erk.* He has shown that it is necessary to add to the viscosity a correcting term

$$-\frac{\rho_1 V}{8\pi T l}\left(m + ln\frac{p_1}{p_2}\right),$$

where m is a constant of value 1·12 and V the volume of gas of density ρ_1 passing through the capillary in time T.

which on substitution for $(\Delta p - \kappa n)$ gives

$$-(p_2{}^2 - p_1{}^2) = K + Ln + Mn^2,$$

where

$$K = (2p - A)\,A\left\{\left(\frac{X}{A^2}\right) + \left(\frac{X}{A^2}\right)^2 + 2\left(\frac{X}{A^2}\right)^3 + \ldots\right\} + X,$$

$$L = 2p\kappa + (2p - A)\frac{Y}{A}\left\{1 + 2\left(\frac{X}{A^2}\right) + 6\left(\frac{X}{A^2}\right)^2 + \ldots\right\} + Y,$$

$$M = \kappa + (2p - A)\left[\frac{Z}{A}\left\{1 + 2\left(\frac{X}{A^2}\right) + 6\left(\frac{X}{A^2}\right)^2 + \ldots\right\}\right.$$
$$\left. + \frac{Y^2}{A^3}\left\{1 + 6\left(\frac{X}{A^2}\right) + 30\left(\frac{X}{A^2}\right)^2 + \ldots\right\}\right] + Z.$$

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* S. Erk, 'Z. Tech. Phys.,' vol. 10, p. 453 (1929).

This expression is deduced on the assumption that the pressures p_1 and p_2 and, therefore, the rate of flow remain constant. In the present case where this assumption is not true, it is justifiable to replace the constant rate of flow by the average value, as the correction is never larger than 0·5 per cent. The term $ln\, p_1/p_2$ involves a very small correction with the present apparatus, as at low pressures $\rho_1 V$ is very small and the whole expression negligible, and at high pressures, when it can be written as approximately $\Delta p/p$, it is small with respect to m.

Results.

The results of the measurements made with nitrogen at 25°, 50° and 75° C. up to 1000 atmospheres, are given in Tables I to III. The pressures are given in international atmospheres, the densities in Amagat units (D_A) and in grams per cubic centimetres (ρ) and the viscosities in c.g.s. units.

Table I.—Viscosity of Nitrogen at 25° C.

Filling and run.		$p_{atm.}$	D_A.	ρ.	$\eta \,.\, 10^6$.	η/ρ.
1	II	10·95	10·05	0·01257	179·4	0·01427
	V	12·71	11·67	0·01460	179·6	0·01231
	III	13·57	12·46	0·01558	179·9	0·01154
	IV	14·44	13·27	0·01659	180·0	0·01085
	I	15·33	14·08	0·01760	180·2	0·01024
13	III	15·36	14·11	0·01764	180·5	0·01023
2	III	48·22	44·37	0·05549	186·4	0·003360
	II	57·59	52·97	0·06624	188·4	0·002844
	I	66·98	61·55	0·07700	190·8	0·002479
3	I	92·31	84·46	0·1056	198·1	0·001876
	II	104·5	95·19	0·1190	200·5	0·001685
	III	118·6	107·5	0·1345	204·9	0·001524
	IV	132·7	119·6	0·1496	209·4	0·001400
4	III	165·5	146·7	0·1834	219·9	0·001199
	IV	174·9	154·1	0·1927	223·1	0·001158
	II	189·0	164·9	0·2063	228·2	0·001106
	I	212·4	182·3	0·2300	236·7	0·001038
6	IV	277·7	226·0	0·2826	258·3	0·000914
	III	320·4	251·2	0·3141	276·4	0·000880
7	I	364·6	274·8	0·3436	294·1	0·000856
6	VI	364·6	274·7	0·3436	294·8	0·000858
	I	387·6	286·1	0·3578	304·0	0·000850
	V	430·2	305·5	0·3821	319·4	0·000836
7	II	430·2	305·6	0·3821	320·9	0·000840
6	II*b*	473·1	323·1	0·4041	337·4	0·000835
7	III	476·1	324·3	0·4055	338·5	0·000835
	IV	541·7	348·2	0·4354	363·4	0·000834
8	I	541·7	348·2	0·4354	365·4	0·000839
7	V	587·7	363·6	0·4548	382·0	0·000840
	VI	630·3	376·6	0·4710	397·4	0·000844
8	II	630·4	376·7	0·4711	399·7	0·000848
	III	742·0	406·5	0·5084	440·4	0·000866
	IV	854·1	432·4	0·5408	480·2	0·000888
	V	965·7	454·5	0·5684	520·5	0·000916

Table II.—Viscosity of Nitrogen at 50° C.

Filling and run.		p_{atm}.	D_A.	ρ.	$\eta \cdot 10^6$.	η/ρ.
13	I	15·37	12·98	0·01623	191·3	0·01179
12	I	57·60	48·37	0·06049	198·1	0·003274
11	II	104·5	86·59	0·1083	208·8	0·001928
10	I	212·4	165·3	0·2067	237·3	0·001148
9	VI	320·4	229·9	0·2875	273·7	0·000952
	IV	430·2	282·1	0·3528	312·9	0·000887
	V	541·7	324·1	0·4053	350·9	0·000866
8	IX	630·4	352·6	0·4409	378·6	0·000859
	VI	742·1	382·7	0·4786	416·5	0·000870
	VIII	854·1	409·2	0·5117	455·0	0·000889
	VII	965·8	432·1	0·5404	491·3	0·000909

Table III.—Viscosity of Nitrogen at 75° C.

Filling and run.		p_{atm}.	D_A.	ρ.	$\eta \cdot 10^6$.	η/ρ.
13	II	15·37	12·03	0·01505	202·2	0·01344
12	II	57·61	44·71	0·05591	208·8	0·003734
11	I	104·5	79·72	0·09970	217·5	0·002181
10	III	212·4	152·1	0·1902	240·8	0·001266
	II	320·3	212·6	0·2659	274·6	0·001033
9	III	430·2	262·8	0·3287	307·9	0·000937
	II	541·7	304·3	0·3806	342·6	0·000900
	I	630·3	332·5	0·4158	370·1	0·000890
8	XII	742·0	362·8	0·4537	401·6	0·000885
	XI	854·1	389·2	0·4867	436·2	0·000896
	X	965·7	412·1	0·5153	470·3	0·000913

In the calculations use was made of the compressibility isotherms given by Bartlett* in his critical survey and estimated by him to have an accuracy not greater than 0·1 per cent. Calculation shows that this figure involves an accuracy of 0·15–0·50 per cent. in the viscosity, according to the size of the mercury head in different runs with any filling. In the experiments it was found that the maximum variations between measurements with different fillings and the same pressure, and therefore with different mercury heads, was 0·50 per cent. On the other hand, with the same filling and the same mercury head the reproducibility was never worse than 1 in 5000.

The results may be extrapolated to 1 atmosphere and reduced to 0° C. by means of Sutherland's relationship, using the value of the constant = 118 given by C. J. Smith*

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* E. P. Bartlett, 'J. Amer. Chem. Soc.,' vol. 49, pp. 694, 1956 (1927); vol. 50, p. 1284 (1928); vol. 52, p. 1363 (1930).

25° $\eta_{1\text{ atm.}} = 177{\cdot}5 \times 10^{-6}$ $\eta_0 = 165{\cdot}6 \times 10^{-6}$

50° $\eta_{1\text{ atm.}} = 189{\cdot}6$ $\eta_0 = 166{\cdot}2,$

75° $\eta_{1\text{ atm.}} = 200{\cdot}0$ $\eta_0 = 165{\cdot}6$

The values reduced to 0° compare favourably with that given by Smith, $\eta_0 = 166{\cdot}5 \times 10^{-6}$, and those by other observers.

Discussion.

The values of the viscosity are plotted against the pressure in fig. 3. It will be seen that at low pressures the viscosity has a positive temperature coefficient $(\partial\eta/\partial T)_p > 0$, whilst at higher pressures, as is the case for liquids $(\partial\eta/\partial T)_p < 0$.

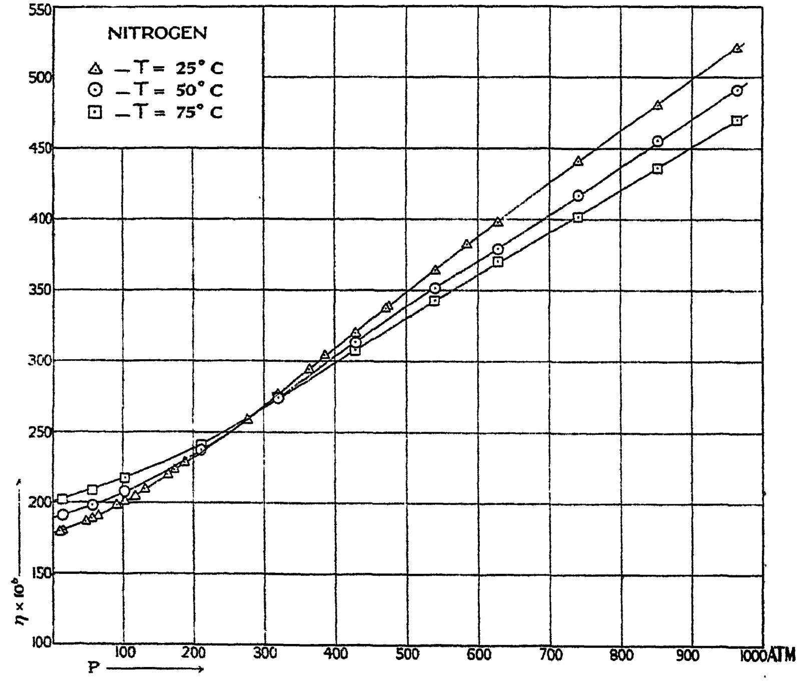

FIG. 3.—Viscosity pressure curves.

If, however, the value of $(\partial\eta/\partial T)_v$ for liquids is calculated from the compressibility data and the temperature and pressure coefficients of viscosity, it appears that this is approximately zero, whilst for a gas it should be positive according to the classical kinetic theory. In fig. 4 the viscosity has been plotted against density. It is seen that $(\partial\eta/\partial\mathrm{T})_v$ is positive and that within the limits of the experimental accuracy, it remains constant over the whole density range,

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* C. J. Smith, 'Proc. Phys. Soc.,' vol. 34, p. 155 (1922).

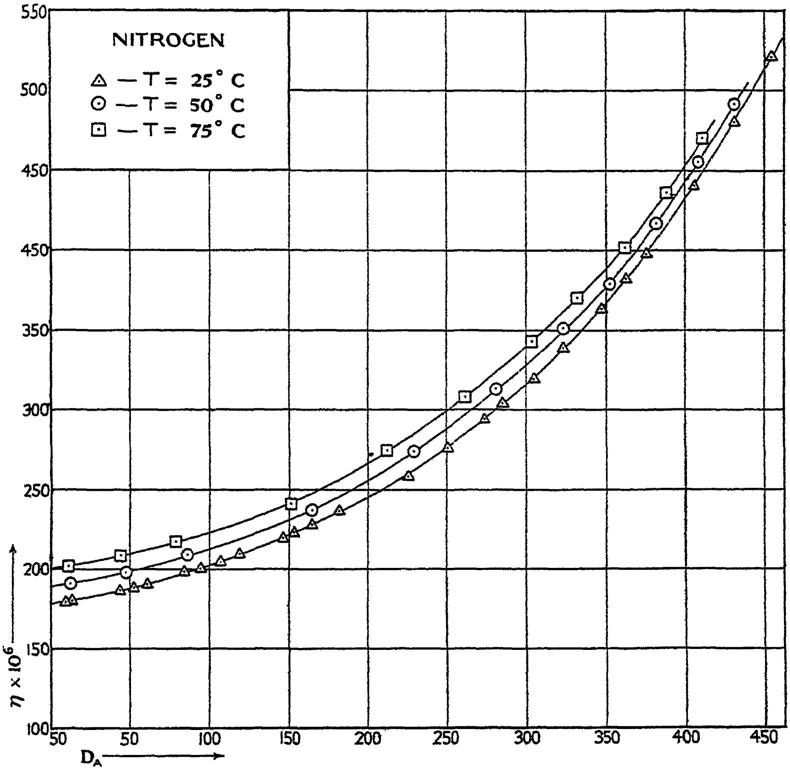

FIG. 4.—Viscosity density curves.

although, of course, the specific temperature coefficient $1/\eta\,(\partial\eta/\partial\mathrm{T})_p$ becomes progressively smaller as the viscosity increases.

A comprehensive theory of the viscosity of compressed gases has been put forward by Enskog.*† He concludes that η/ρ plotted against ρ must give a minimum and that the curve must satisfy the equation

$$\frac{\eta}{\rho} = \frac{1}{2\cdot545}\left(\frac{\eta}{\rho}\right)_{\text{min.}}\left[\frac{1}{b\rho\kappa} + 0\cdot800 + 0\cdot7614\, b\rho\kappa\right], \qquad (11)$$

where $b\rho\kappa$ is obtained from his equation of state for compressed gases

$$p + a\rho^2 = \frac{\mathrm{RT}}{\mathrm{M}}\,\rho\,(1 + b\rho\kappa),$$

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* D. Enskog, "K. Svenska Veten. Hand.," vol. 63, No. 4 (1922). See also J. D. van der Waals, Jr., "Versl. Akad. Wet.," Amsterdam, vol. 27, p. 744 (1918).

† The authors are indebted to Professor Lennard Jones for drawing their attention to the importance of Enskog's work in relation to their own.

and can be calculated from isotherm data on the assumption that a, b and κ are all independent of temperature. In this case

$$b\rho\kappa = \frac{\mathrm{T}\dfrac{dp}{d\mathrm{T}}}{\dfrac{\mathrm{RT}}{\mathrm{M}}\rho} - 1.$$

In fig. 5 the experimental values of η/ρ against ρ show the existence of these minima.

Equation (11) was checked by calculating $b\rho\kappa$ from the values given by Deming and Shupe* based on Bartlett's results, and by using the values of $(\eta/\rho)_{\text{min.}}$ obtained from the above curves.†

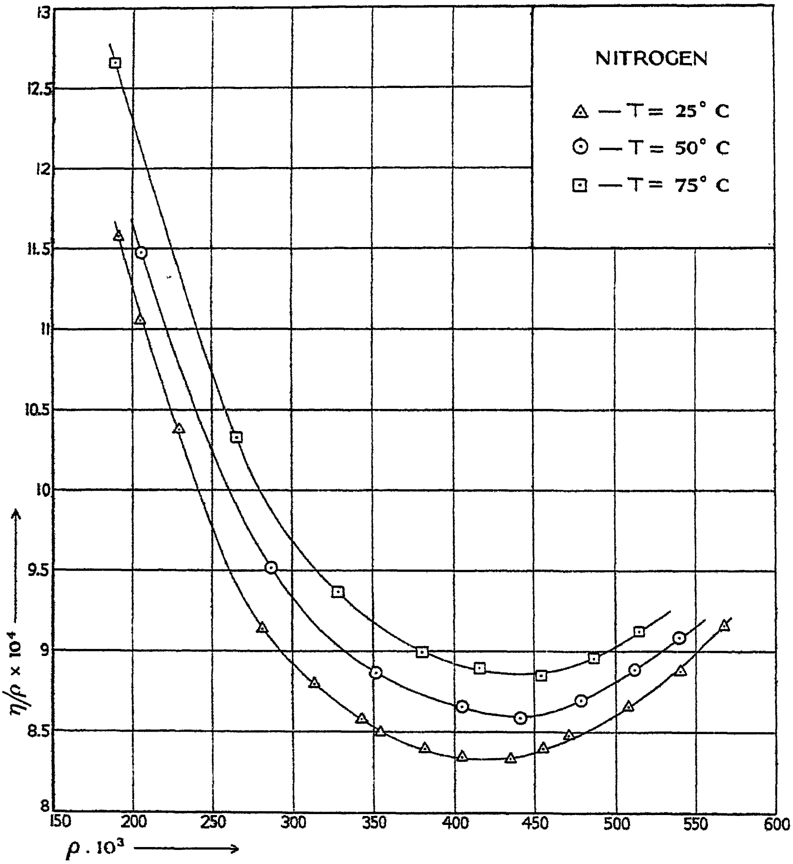

Fig 5.

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* W. E. Deming and Lola E. Shupe, 'Phys. Rev.,' vol. 37, p. 638 (1931).

† It was possible to put a smooth curve through all the values calculated from Deming and Shupe's figures except that at 700 atmospheres. This point was neglected and the value from the curve was used.

The calculated and experimental values of η for 50° C. are given in Table IV.

Table IV.

$p_{\text{atm.}}$	$b\rho_{K}$	$\eta \cdot 10^{6}_{\text{calc.}}$	$\eta \cdot 10^{6}_{\text{exp.}}$
15·37	0·031	181	191·3
57·60	0·119	190	198·1
104·5	0·215	205	208·8
212·4	0·491	224	237·3
320·4	0·717	266	273·7
430·2	0·920	308	312·9
541·7	1·111	348	350·9
630·4	1·247	380	378·6
742·1	1·413	418	416·3
854·1	1·576	455	455·0
965·8	1·732	492	491·3

Enskog's theory also leads to a formula for the diameter of the gas molecule

$$s = \frac{1}{0{\cdot}955}\sqrt{\frac{M}{RT}}\left(\frac{\eta}{\rho}\right)_{\text{min.}}$$

Substitution of the experimental values gives the following results for nitrogen :

$$T = 25^\circ \qquad S = 2{\cdot}97 \times 10^{-8}\ \text{cm.}$$

$$T = 50^\circ \qquad S = 2{\cdot}94 \times 10^{-8}\ \text{cm.}$$

$$T = 75^\circ \qquad S = 2{\cdot}92 \times 10^{-8}\ \text{cm.}$$

Summary.

In the present paper a description is given of a method for measuring the viscosities of gases at high pressures. The method depends on the transpiration of gas through a capillary. A detailed account is given of the apparatus and of the method of calculating the viscosity from the experimental data.

Results are given for the viscosity of nitrogen at 25°, 50° and 75° C. up to 1000 atmospheres.

In conclusion, the authors wish to express their thanks to Imperial Chemical Industries, Ltd., for grants, which enabled this work to be undertaken, and for enabling one of them (R.O.G.) to participate in it. They are also indebted to several assistants of the Physical Laboratory of the University of Amsterdam and members of the Research Department of Brunner, Mond & Co., Ltd., who have assisted with the experimental work and with the calculations.

The Theory of Metallic Corrosion in the Light of Quantitative Measurements. Part V.—The Corrosion of Iron and Mild Steel.

By G. D. Bengough, A. R. Lee, and F. Wormwell.

(Communicated by Sir Harold Carpenter, F.R.S.—Received August 25, 1931.)

[Plates 3–6.]

The measurement of corrosion by the oxygen-absorption method developed for zinc has now been applied to iron. Since the corrosion products contain mixtures of ferrous and ferric compounds, analyses must be made at the end of various corrosion periods to determine the proportions of oxygen used in corrosion and in the secondary oxidation to the higher valency. Notwithstanding this additional operation, the corrosion measurements have nearly the same order of reproducibility as those for zinc except in special conditions which will be noted later.

Three materials have been used, namely :—

(1) Highly purified iron prepared by electro-deposition and subsequently melting *in vacuo* in a high frequency furnace.

(2) Mild steel made in the usual way for tube manufacture, but specially examined for homogeneity.

(3) An ordinary sample of mild steel rod taken from a workshop store.

The purified iron was prepared for the authors in the Metallurgical Department of the National Physical Laboratory under the direction of Dr. Rosenhain. Electro-deposited iron was compressed and melted *in vacuo* and then in a current of hydrogen to remove oxygen ; the small lumps so produced were remelted to form one large one, which was forged down to a rod 1½ inches in diameter. The analysis of the resulting metal is given in Table I ; experiments numbered FP1 to FP5 were made on this material. Since only a small supply of highly purified iron was available, it was decided to obtain a much larger amount of mild steel made as homogeneous as possible in good industrial tube practice, aided by special examination and selection at several stages of manufacture. This material was made for the authors by Mr. W. H. S. Dickenson in the Vickers Works of the English Steel Corporation ; it has been found to be sufficiently uniform to give satisfactory reproducibility in corrosion

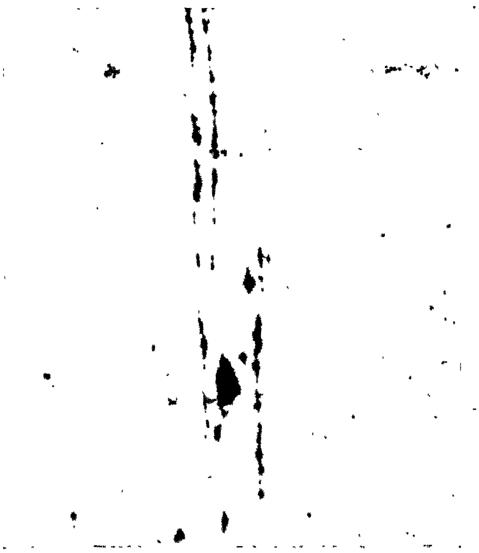

Fig. 1.—Standard Steel, F.S. Long. Sect. Unetched (× 300).

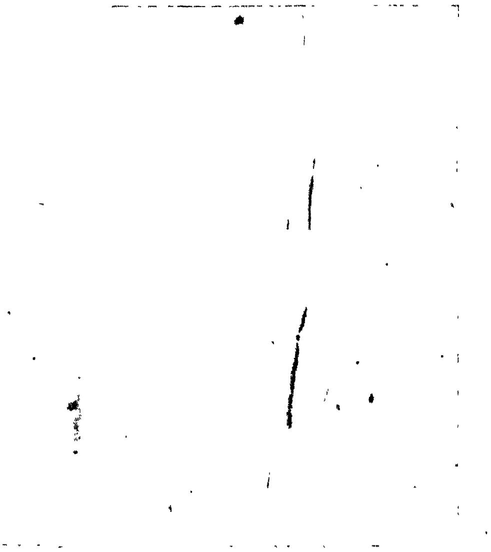

Fig. 2.—Commercial Steel, F. Long. Sect. Unetched (× 300).

Reduced by 25 per cent.

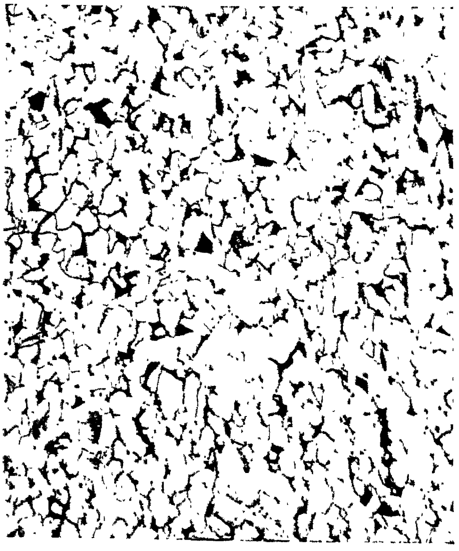

Fig. 3.—Standard Steel, F.S. Long. Sect. Etched (× 100).

Fig. 4.—Commercial Steel, F. Long. Sect. Etched (× 100).

Reduced by 25 per cent.

(*Facing p.* 309.)

experiments and is being used as a standard of reference. Full details are therefore given of its method of manufacture in the Appendix I.

Analyses of the materials used are given in Table I and photomicrographs in figs. 1 to 4 (Plate 3). For these the authors are indebted to the Metallurgical Department of the National Physical Laboratory. It will be noted that the photomicrographs show distinctly less slag in the steel taken from stock than in the specially prepared mild steel, but this is probably a chance effect due to the particular section photographed; it has not yet been found possible to prepare a suitably etched micrograph of the purified iron.

The corrosion tests were performed similarly to those for zinc. The metal specimens were discs 2·5 cm. in diameter and 0·6 cm. thick, which had been turned to size in a precision lathe with a fine last cut. A final annealing after turning was found to be unnecessary to secure good reproducibility, although this had been essential with zinc. The discs were immersed in 100 c.c. of liquid beneath an atmosphere of oxygen with the upper surface 1·5 cm. below the waterline; the temperature and pressure were 25° C. and 760 mm.

Table I.—Analyses of Materials Used.

	Purified iron. Mark FP.	Selected mild steel. Mark FS.	Commercial mild steel. Mark F.
	Per cent.	Per cent.	Per cent.
Carbon	0·018	0·13	0·11
Silicon	0·003	0·15	0·07
Sulphur	0·0015	0·034	0·037
Phosphorous	0·003	0·034	0·030
Manganese	Trace	0·46	0·56
Nickel	Nil	0·20	Nil
Chromium	Nil	0·04	Nil
Copper	Nil	0·05	—
Oxygen	0·071	0·02	—

Method of Obtaining Corrosion-time Curves.

Fig. 6A shows typical curves for true oxygen absorption against time for the standard steel. Hydrogen gas was evolved throughout the experiments and the observed oxygen absorption has been corrected for this in a similar way to that used for zinc. The curves are not corrosion-time curves, since part of the oxygen absorbed has been used for oxidation of corrosion products to a higher valency. To correct for this the ferrous and the total iron corroded were determined at the end of each experiment and this enabled a final point on a true corrosion-time curve to be ascertained.

The calculation is as follows :—

Let the total loss of weight due to corrosion = W grams.

Then $W = W_0 + W_H$, where W_0 = weight lost by oxygen corrosion, and W_H = weight lost by displacement of hydrogen gas.

Let volume of oxygen required to oxidise W_0 to ferrous state = V c.c. (*a*)

Also let p = fraction of total corroded iron found in the ferrous state in the corrosion product at the end of the experiment.

Then $(1 - p)\,W_0$ = weight oxidised to ferric state.

Therefore volume of oxygen required to oxidise it from ferrous to ferric state =

$$(1 - p)\,V/2 \text{ c.c.} \qquad (b)$$

Let volume of hydrogen evolved corresponding to W_H = H c.c.

Then volume of oxygen equivalent to W_H = H/2 c.c., (*c*)

and weight of iron oxidised from ferrous to ferric state = $(1 - p)\,W_H$.

Therefore volume of oxygen required for this oxidation

$$= \tfrac{1}{2}(1 - p)\,H/2 = \tfrac{1}{4}(1 - p)\,H. \qquad (d)$$

Let T = the total observed volume of oxygen absorption = (*a*) + (*b*) + (*d*). Then

$$T = V + (1 - p)\,V/2 + H/4\,(1 - p),$$

and

$$T + H/2 = V + (1 - p)\,V/2 + H/2 + H/4\,(1 - p)$$
$$= (V + H/2)\,(3/2 - p/2),$$

or

$$V + H/2 = \frac{T + H/2}{1\cdot5 - p/2}.$$

Let $V' = V + H/2$ = total corrosion expressed as cubic centimetres of oxygen.

Then $V' = \dfrac{T'}{1\cdot5 - p/2} = \dfrac{2T'}{3 - p}$, where $T' = T + H/2$.

The point obtained for the corrosion-time curve is based on an oxygen absorption measurement T, a hydrogen gas measurement H and a determination of p, that is, the fraction of the total iron remaining in the ferrous state at the time of the observations. But p can only be determined at the end of the experiment, and it cannot be assumed to be constant throughout. Hence a series of corrosion experiments must be made to determine p at different times, so that a curve can be constructed showing the effect of time on p.

In order to determine *p*, the specimen with adherent corrosion product was left overnight in a de-aerated saturated solution of boric acid. This loosened the corrosion products (as originally suggested by Friend) and they were then brushed off with a stiff brush so as to leave bare metal which could be weighed after drying. The corrosion products were washed into a beaker with boiled distilled water, acidified with sulphuric acid and heated to obtain a clear solution. Portions were then titrated with N/100 potassium permanganate. Other portions were reduced with stannous chloride and titrated with potassium bichromate to obtain the total iron. This agreed well with loss of weight measurements. An error of 3 per cent. in the value of *p* causes an error of about 1 per cent. in the calculated corrosion.

Nature and Properties of the Precipitated Corrosion Product.

Fig. 5 shows the results of experiments on the corrosion products from standard steel in conductivity water, N/10,000 and N/10 KCl. Most of the points obtained in N/10,000 KCl lie on one of two nearly parallel curves which show that the proportion of ferrous iron increases with time up to about 150 days, after which it becomes nearly constant. The factors which appeared to decide the curve on which the results of an experiment would fall were changes in the configuration of mounds of corrosion products which formed on the surface of the metal; they will be discussed later.

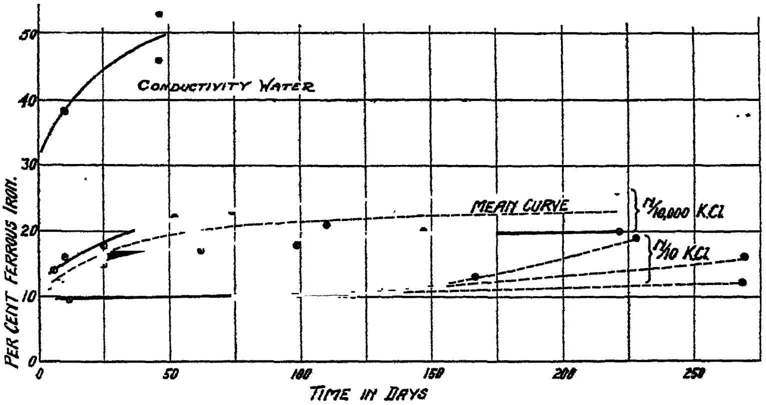

FIG. 5.—Per cent. ferrous curves.

The mounds had considerable influence on the corrosion rate and were formed in dilute solutions when an oxygen atmosphere was used. With purified air they were less definite and more fragile. In ordinary air they were not formed at all and the corrosion products were largely flocculent. In N/10 KCl and stronger solutions, mounds were never formed and the corrosion products were always flocculent.

In all the solutions the corrosion products consist partly of loose brown hydrated ferric oxide, some of which is in the magnetic γ form. This has no effect on the corrosion rate even when the metal specimen is completely embedded in it; thus, specimens FS8 and 9 in N/10 KCl showed straight line corrosion-time curves for 250 days (similar to FS5 in fig. 6) and no change in corrosion rate occurred when the ferric oxide was shaken off the metal, though the latter was corroding under conditions of oxygen control. Part of the ferric oxide is precipitated in the form of transparent glassy films, sufficiently thin to show interference colours and strongly adherent either to the metal surface or the glass walls of the corrosion vessels. This form is highly protective in weak chloride solutions, but only temporarily in strong solutions. It plays an important part in the distribution of corrosion.

Much of the corrosion product is in the form of black magnetic oxide which is quite stable in the presence of oxygen. Forrest, Roetheli and Brown* have shown that this can be produced :—

(1) By adding sodium hydroxide to mixed solutions of ferrous ammonium sulphate and ferric chloride.
(2) By mixing gelatinous precipitates of ferrous and ferric hydroxide suspended in water.
(3) By aerating ferrous hydroxide suspended in water.

They give no analyses of the substance formed either artificially or in corrosion experiments, but state that it is magnetic and that the X-ray spectrographs of the black precipitated oxides formed by methods (2) and (3) were similar to that of black magnetic oxide of iron. This is not conclusive since the spectrograph of the γ (magnetic) form of red ferric oxide is similar to that of the black magnetic oxide and differs only in relative intensity of the lines. Analyses have been made by the present authors of the black oxide formed in actual corrosion experiments after careful separation from the red oxide by mechanical means, and these showed 34·9 and 34·6 per cent. of ferrous iron as against 33·3 per cent. for pure magnetite. It seems clear that the stable black oxide formed in corrosion experiments may be identified with the mineral magnetite.

Forrest and his colleagues conclude that " a corrosion product of precipitated ferrous hydroxide will be formed at ferrous-ion concentrations such as are found in corrosion processes, only when the p_H in the film is high," such as p_H 8·5 to 11, and that "ferrous hydroxide when formed will react with ferric hydroxide to form granular magnetic oxide of iron."

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* Forrest, Roetheli and Brown, 'Industrial & Engineering Chemistry,' vol. 23, p. 651 (1931).

General Forms and Reproducibility of Corrosion-time Curves.

The calculation of a corrosion-time curve from the experimental results was based on that one of the curves shown in fig. 5 upon which fell the value of p determined at the end of the experiment. Such corrosion-time curves are FS2, 3 and 5 in fig. 6 which were obtained from the oxygen absorption curves shown in fig. 7A.

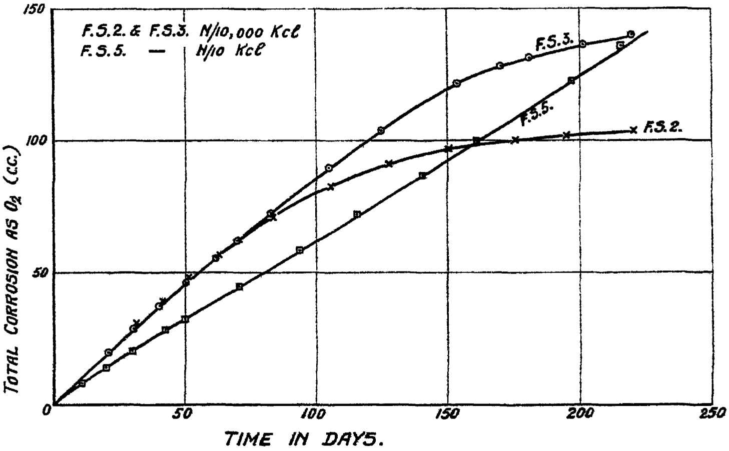

FIG. 6.—Corrosion-time curves N/10,000 and N/10 KCl.

Table II gives some comparative results obtained on the same specimens by the oxygen-absorption and the loss of weight methods of measuring corrosion. The latter usually gives a lower result than the former, probably because of incomplete removal of corrosion products. The agreement is of the same order as that found for zinc, and shows that the necessity of determining the percentage of ferrous iron in the corrosion product does not introduce any serious error.

Two types of curve have been observed, one characteristic of the range conductivity water to N/10,000 KCl, the other of the range N/10 to 4N; between them transition types were found. Associated with these two ranges are two distinct types of corrosion product.

In the first range the corrosion product is found in the form of flat hollow discs or mounds which adhere to the surface of the specimen and very little

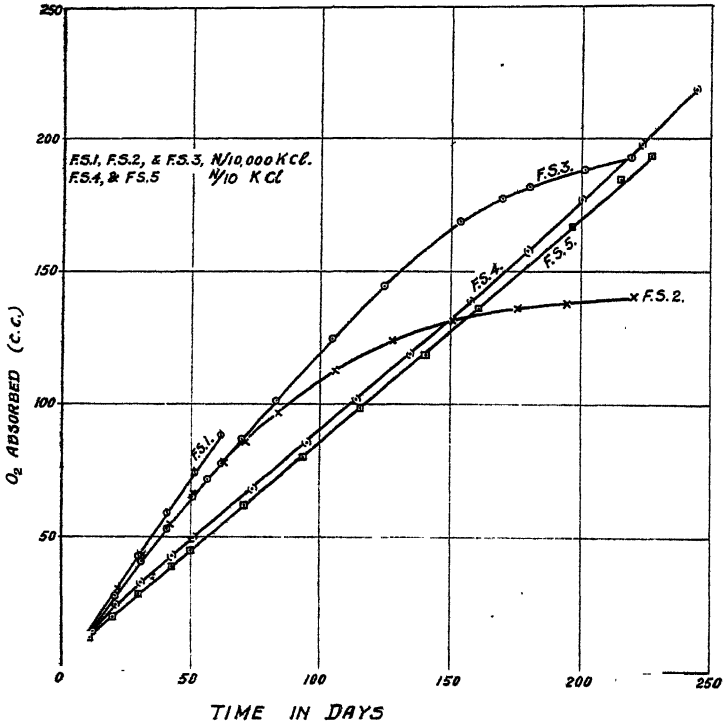

Fig. 6a.—Oxygen absorption curves N/10,000 and N/10 KCl.

Table II.—Comparison between the Oxygen Absorption and Loss of Weight Methods.

Experiment.	Solution.	Time of corrosion.	Loss of weight.	Calculated from oxygen absorption.
		days	mgrms.	mgrms.
FS12	Conductivity water	45	19·1	18·4
FS25	N/1,000,000	57	73·0	80·0
FS1	N/10,000	62	286·8	288·0
FS2	N/10,000	221	458·1	472·8
FS14	N/1000	105	368·9	377·4
FS16	N/200	93	336·6	331·9
F6	N/10	120	345·7	345·4
FS5	N/10	228	650·9	653·5
FS13	N	181	373·3	376·5
FS7	4N	60	46·3	49·4

of it falls to the bottom of the corrosion vessel. In the early stages of the experiments these mounds show wide openings which become gradually narrower as corrosion proceeds.

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——————, garnet, production for quinquennial period 1909-13. L. L. F., XLVI, 271; 1914-18. E. H. P., LII, 291; 1919-23. LVII, 355.

——————, geological traverse. R. B. F., XVIII, 12, 25 (Pls. i, ii).

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In the strong solution range no mounds are formed. Much of the brown corrosion product is loose and falls to the bottom of the vessel, but part forms a layer on the top surface and sides of the specimen. The bottom surface becomes covered after a time with a thin black layer which also underlies the brown layer on the corroded part of the top surface and sides.

The degree of reproducibility of corrosion rates varies according to the solution. In general, reproducibility in weak solutions is best during the initial periods of corrosion, whereas in strong solutions it is worst during these periods. Examples of this are shown in fig. 6A. The two specimens FS2 and FS3 in N/10,000 KCl gave identical curves for the first 70 days, but after that they commenced to diverge and at 200 days FS3 had given about 30 per cent. more corrosion than FS2. Fig. 8 shows curves for specimens of commercial steel F; the oxygen absorption values in N/10,000 KCl differ by ±1·5 per cent. from the mean up to about 270 days. The curves for FS4 and FS5 in N/10 KCl (fig. 6A) show identical slopes from 25 to nearly 250 days. This is fairly characteristic of all strong solutions, though during the first 20 to 50 days the slopes in N/10 KCl may occasionally differ as much as ±10 per cent. from the mean. Table III gives some characteristic rates of corrosion over the initial periods for N/10,000 KCl solutions and over the later periods for N/10 KCl. It will be noticed that the standard steel (FS) gives a faster rate than the commercial (F) in both solutions. The pure iron (FP) gives the slowest rate in N/10,000 KCl, but an intermediate rate in N/10. These figures seem to indicate that in addition to distinguishing between iron and zinc the experimental procedure adopted in this research shows certain differences in the corrosion of two types of steel and a sample of pure iron which are corroding under similar external conditions. It was noted that the rate of hydrogen evolution from pure iron was less than that from the steels.

Table III.—Total Corrosion (in terms of Oxygen absorbed per day).

N/10,000 KCl.		N/10 KCl.	
Specimen.	Rate, c.c. per day.	Rate, c.c. per day.	Specimen.
F12	0·99	0·57	F4
F11	0·99	0·55	F6
FS2	1·06	0·60	FS4
FS3	1·06	0·59	FS5
FP3	0·84	0·59	FP1
FP4	0·70	0·58	FP2

Corrosion-time Curves in Conductivity Water.

Both varieties of steel gave exponential curves of the type $y = A\,(1 - e^{-kt})$ in conductivity water; curves for standard steel are shown in fig. 5 together with the derived curves. A curve for the commercial steel was found to lie wholly above those for the standard steel, and all three showed corrosion rates much faster and longer sustained than those found for zinc, one of which is shown dotted in fig. 7.

The two curves for the standard steel are in good agreement for about 12 days, after which they diverge owing to the observed differences in behaviour of the mounds of corrosion products which stayed open longer on specimen FS11.

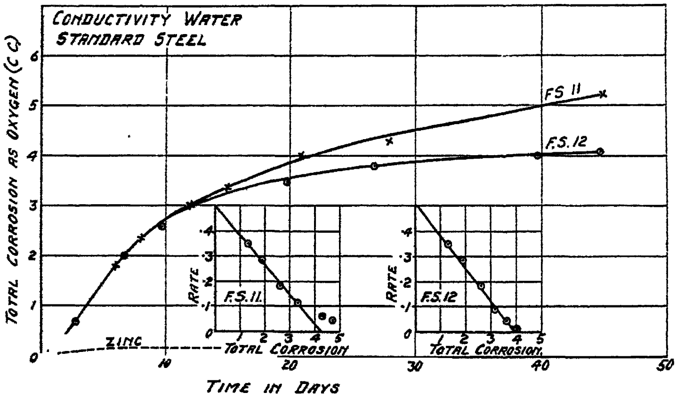

FIG. 7.—Oxygen absorption time curves. Conductivity water.

These mounds exercise a determining effect on corrosion rates and reproducibility in all liquids from conductivity water to about N/1000 KCl. As the concentration rises they become less conspicuous and in N/10 KCl have disappeared altogether.

An experiment on the pure iron specimen FP5 showed that the initial corrosion rate was nearly the same as that for mild steel, *e.g.*, at the end of 4 days pure iron showed an oxygen absorption of 1·2, whereas standard steels FS11 and 12 showed 1·6. However, the pure iron maintained its corrosion rate better, and at the end of 40 days the oxygen absorption was 13 c.c. as against 6·2 c.c. for FS11 and 9·7 c.c. for a sample of commercial steel. These differences seem to be due to the behaviour of the mounds of corrosion product, but shortage of material prevented the repetition of the experiment with pure iron, so that its behaviour in the above experiment cannot be described as typical.

Effect of KCl *Concentration on Corrosion.*

Curves for oxygen absorption and total corrosion in N/1,000,000 KCl are similar to those in conductivity water, *i.e.*, exponential in form. Curves in N/100,000 KCl for oxygen absorption and total corrosion seem to take a form intermediate between those for conductivity water and N/10,000 KCl. The form of corrosion-time curve of F12 in N/10,000 KCl corresponding to the oxygen-absorption curve of fig. 8, has been investigated up to the point A and has been found to conform with the equation $y = k \tanh t$ where y is the total corrosion at time t. This is a hyperbolic tangent, as shown by fig. 9, which is the curve derived from the corrosion-time curve by plotting dy/dt against y^2, *i.e.*, the rate of corrosion against the square of the total corrosion. This is a straight line and accords with the equation above.

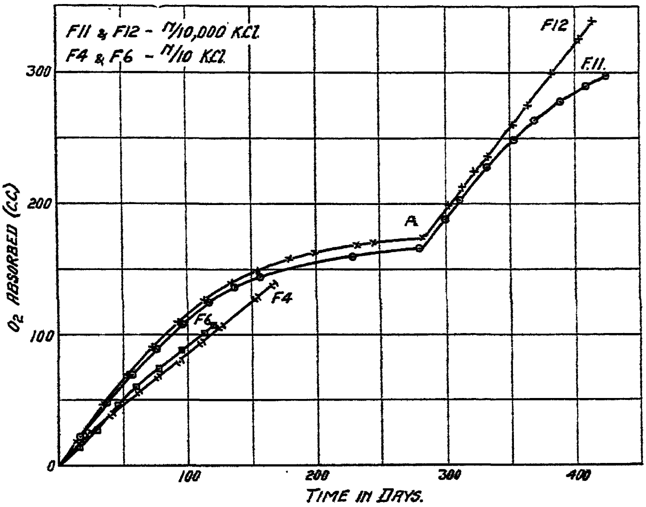

FIG. 8.—Oxygen absorption commercial steel.

In previous papers it has been shown that zinc in N/10,000 KCl solution gives an exponential corrosion-time curve. The factor which dictated the curve-form for zinc was the rate of diminution of chloride ion concentration in the solution. This is not the case with iron or steel, since no appreciable diminution of concentration could be detected even when the corrosion rates had fallen to less than one-fifth of the original rates.

It was thought possible that the decrease in the corrosion rate might be caused by the accumulation of corrosion products. To test this view two of the experiments recorded in fig. 8 were interrupted at the end of 283 days, shown at point A on the curves, and the corrosion vessels opened; the mounds of corrosion product were then removed with a glass rod as far as possible, but the specimen was never allowed to dry. The apparatus was next swept out with purified oxygen, sealed up again, replaced in the thermostat and oxygen absorption and hydrogen evolution measurements were then continued as before. The new curves are shown in fig. 8 to the right of A; they closely reproduced the initial curves until the varying behaviour of the mounds of corrosion products caused divergence.

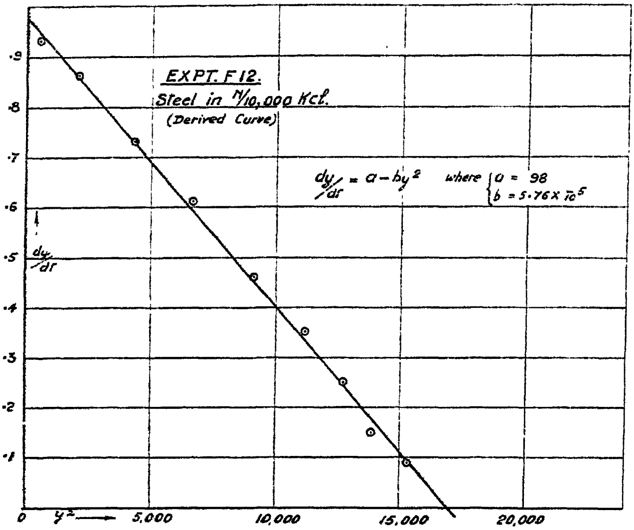

FIG. 9.—Derived curve dy/dt and y^2.

Experiments were made on specimens FS2 and 3 to determine whether the experiments in N/10,000 KCl solutions, such as those illustrated in figs. 6 and 6A, were under oxygen control as defined in a former paper.* Convection currents induced in the corrosion vessel caused increased corrosion rates for the initial portions, but not for the flattened later parts of the curve which correspond to corrosion rates less than one-tenth of the initial rates. Consequently, oxygen control only holds over the earlier part of the experiments, when the oxygen concentration will be low in the proximity of the mounds. Over the later part of the curve when the corrosion rates are small this oxygen concentration will be high and consequently relatively unaffected by convection currents.

According to the differential aeration principle, if the mounds of corrosion product were acting as oxygen screens the corrosion rates would not be expected to fall off to the extent actually observed, for on this theory corrosion would be carried on by oxygen reaching the bright metal outside the mounds, which has been observed to remain practically constant at about 50 per cent. of the whole surface area throughout the experiment. The form of curve cannot be explained by increase in resistance of the liquid path, since it has been found that the initial corrosion rates are independent of conductivity in this range of solution. If the effect of conductivity were being masked by oxygen control as determined by the apparatus then there should be an initial straight line portion of the corrosion-time curve in N/5000 KCl.* This should persist until the resistance had increased beyond the initial value for N/100,000 KCl. Actually there is no straight line portion for this curve, which is identical with that for N/10,000 KCl (FS3 of fig. 6A).

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* 'Proc. Roy. Soc.,' A, vol. 127, p. 44 (1930).

The following facts have been ascertained about the factors which influence the fall of corrosion rate indicated by the corrosion-time curves in these dilute solutions :—

(1) The fall is not due to diminution in chloride ion concentration in the solution such as occurred with zinc.

(2) The fall is not due to any changes at, or reduction in size of, unattacked areas.

(3) The initial rates in solutions between N/100,000 and N/1000 are independent of the concentration and, therefore, of the conductivity of the liquid, which does not appear to exert a controlling influence.

(4) The fall of corrosion rate is accompanied by the gradual closing of the openings of the corrosion mounds; if these do not close the rate does not fall. If a closed mound is removed the corrosion rate rises to its initial high value.

It seems reasonable to assume that the corrosion rate is determined by the area of the opening of the mounds.

On this assumption it can be shown that if these build up in the form of cones or flat discs an exponential curve of the type $y = \mathrm{A}(1 - e^{-kt})$ would be expected; if they build up in the form of hemispheres then the hyperbolic curve $y = k \tanh t$ would be expected. The argument for this is given in Appendix II which deals with ideal cases, close agreement with which is occasionally found.

The mechanism of the process appears to be as follows. The whole of the corrosion occurs beneath the mounds and may be carried on by (*a*) the oxygen which enters the openings and (*b*) that which reaches the film-covered unattacked areas. As the openings contract the (*a*) supply is reduced and the corrosion rate falls notwithstanding that oxygen can still obtain free access to the unattacked areas which constitute about 50 per cent. of the total area of the metal surface. Finally the rate falls to less than one-twentieth of the initial rate and it is therefore evident that this fall must be due mainly to some change at the corroding surface. Possibly this consists of anodic polarisation due to the formation at this surface of a film of ferrous hydroxide which offers a mechanical obstruction to the entrance of iron ions into solution. Such a film would be broken down and allow corrosion to proceed at a rate determined by the rate at which oxygen enters the opening of the corrosion mounds.

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* *Cf.* 'Proc. Roy. Soc.,' A, vol. 121 (1928), fig. 4.

The corrosion-time curve for pure iron in N/10,000 KCl is shown in fig. 10.

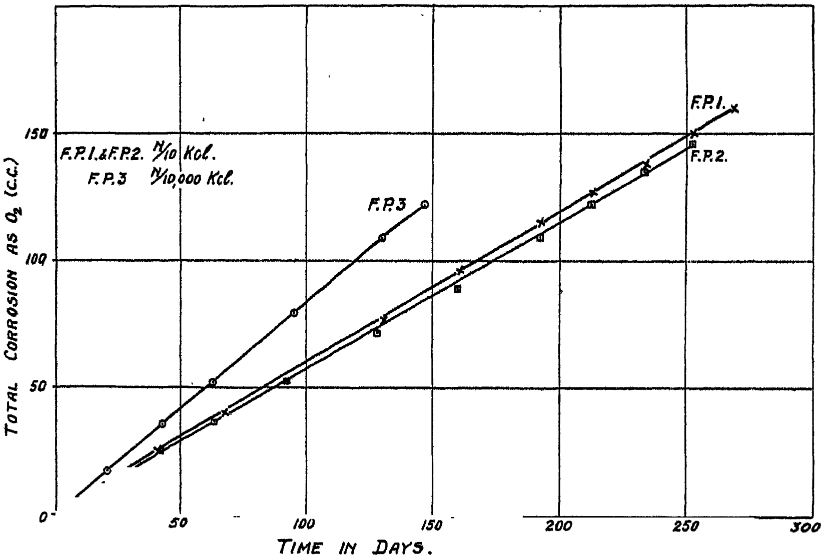

FIG. 10.—Total corrosion—pure iron.

This is a straight line for nearly 150 days, giving a corrosion rate somewhat less than the initial rate for the standard and commercial steels in a similar solution. It cannot be assumed that this type of curve is characteristic for pure iron in weak solutions, as it is dictated by the configuration of the corrosion mounds, which is liable to vary in different experiments, and these mounds may give rise either to a straight line or to a curve involving an exponential function.

A set of corrosion-time curves for different concentrations of KCl is given in fig. 11. It will be noticed that as the concentration is increased the forms of the curves change from exponential to linear. This change is intimately

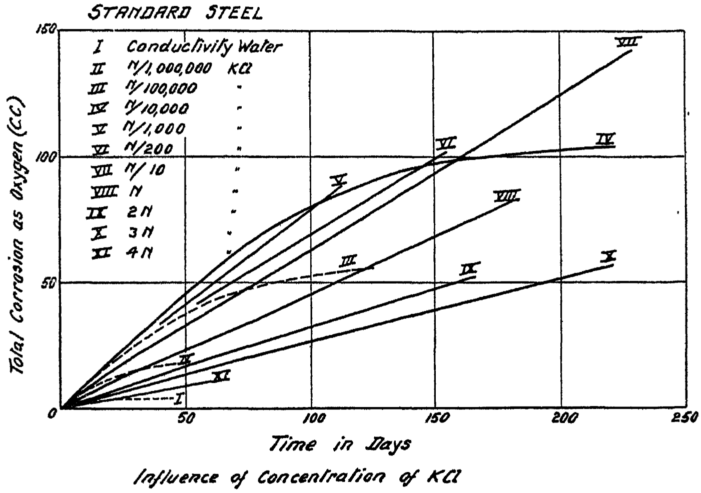

FIG. 11.—Total corrosion curves (full set).

connected with a change in the type of corrosion product, which has been already described. In the strong solutions the brown and black oxides have little or no effect on the rate of corrosion, as was shown by specimens FS8 and FS9 in N/10 KCl, which, after being shaken free from them, continued to give the same rate of corrosion as before. Moreover, certain specimens, such as FS4 which was corroded in N/10 for over 500 days, became completely embedded in corrosion products, so that no metal could be seen, and yet the corrosion-time curves remained straight lines after the usual slight bend at the end of 20 days. Clearly, the accumulation of ferric and black magnetic oxides on iron in N/10 and stronger solutions does not affect appreciably the access of oxygen to the metal, *i.e.*, they behave similarly to the white flocculent corrosion products on zinc and not as oxygen screens. It is evident that the view put forward on p. 116 of Part II of this research, that the fundamental potential responsible for corrosion is due to the local exclusion of oxygen from the metal by accumulation of such corrosion products, is no longer tenable.

The transition between this loose flocculent form of corrosion product and the compact oxygen-excluding type occurs in the region of N/1000 KCl, in which solution the corrosion product usually first appears in the second form and later changes to the first. This change is accompanied by corresponding variations in the corrosion rate. A comparison of the curves for N/10,000 and

N/10 KCl in figs. 11 and 20 shows that mild steel corroded initially (excluding the first day) much faster in the weaker solution, and for 160 days gave more total corrosion. Eventually, however, the rate in that solution decreased to such an extent that the two curves crossed and at 220 days the total corrosion in N/10 was 30 per cent. greater than in N/10,000. This difference would continuously increase for longer periods of corrosion. In atmospheric air, in which no "mounds" are formed, the corrosion rates are nearly identical in the two solutions.

It will be noticed that each of the curves for N/200, N/10 and N KCl, is made up of two straight lines of different slopes. In N/10 for both pure iron and steel the slope of the first part varies in different experiments with the same material, but it may give a rate of oxygen absorption of 1·2 c.c. per day and persists for 20 to 50 days; the slope of the second part is characteristic of a given steel and shows good reproducibility at a rate of about 0·8 c.c. per day (see figs. 6A and 10). The abrupt change in slope would lead to confusing results from loss of weight experiments taken over arbitrary periods of time, *e.g.*, the total oxygen absorption expected for 100 days as calculated from the rate during the first 20 days of FS4 (fig. 6A) would be 115 c.c.; actually the absorption was only 90 c.c. Similarly for FS13 in N solution, the expected figure would be 70 as compared with an actual figure of 62 c.c.

The last two paragraphs emphasise the importance of obtaining continuous corrosion-time curves over considerable periods of time. Except for some by Heyn and Bauer,* Chappell,† and W. D. Richardson,‡ all done by rather crude methods without separate determination of hydrogen gas, the literature is surprisingly bare of such curves in neutral salt solutions.

Figs. 12 and 13 give curves showing the effect of concentration of KCl on the corrosion rate and oxygen absorption for the standard steel in standard conditions. For conductivity water and weak solutions the rates are obtained from the tangents to the first part of the curves; for the solutions giving straight line curves, that part of the curve has been taken which gives the characteristic, most reproducible and longest continued slope, *i.e.*, the later slope.

Fig. 13 shows the curves plotted using logarithmic values of the concentrations. Each curve consists of four branches. Starting from conductivity water the first branch extends up to N/100,000 KCl and is controlled by the concentration. The second branch extends from N/100,000 to approximately

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* Mitteil, 'König. Materialprüfungsamt,' vol. 26, p. 1 (1908).

† 'J. Iron and Steel Inst.,' vol. 85, p. 270 (1912).

‡ 'American Inst. Chem. Eng.,' vol. 13, p. 169 (1920).

N/5000* and is controlled by the oxygen supply as dictated by the dimensions of the vessel, etc. The third branch extends approximately from N/5000 to

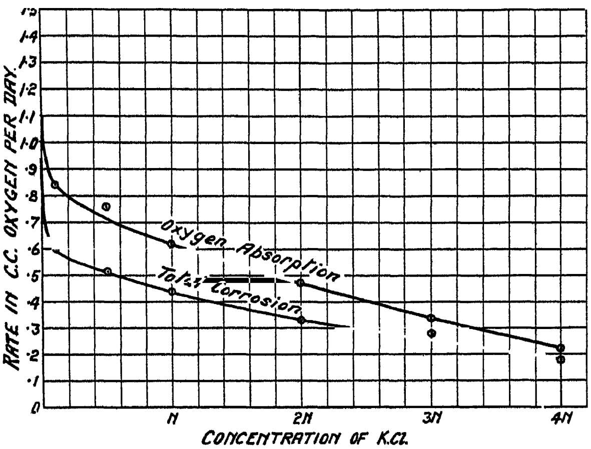

FIG. 12.—Rate of corrosion—conc. KCl.

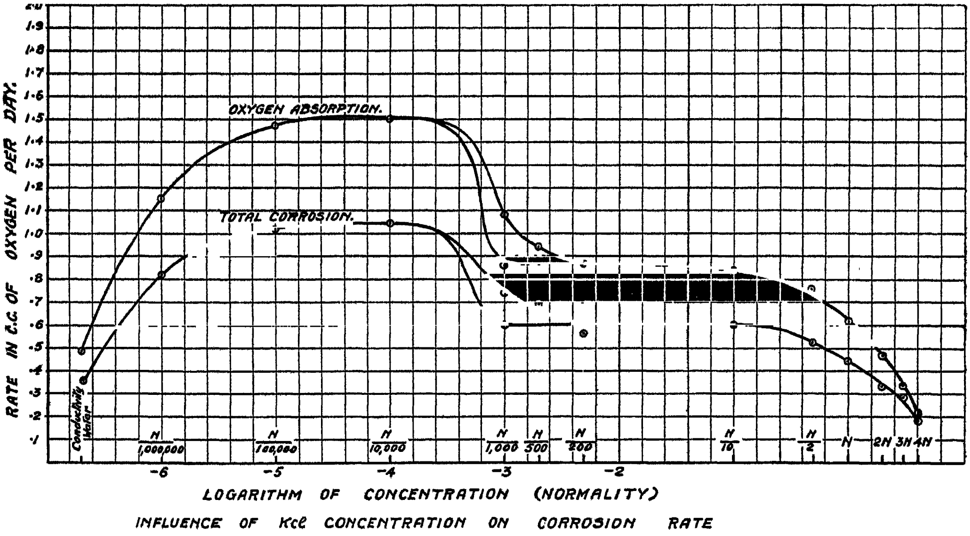

FIG. 13.—Rate of corrosion—log. conc. KCl.

N/200; in this range the corrosion products may take the form characteristic of either dilute or strong solutions and may even change during the course of a single experiment. The particular form dictates the corrosion rate which is liable to vary, and the curve cannot be defined accurately in this region. The fourth branch extending from N/200 to 4N is controlled by the rate of oxygen supply; the fall in corrosion rate as the concentration is increased is due to the decrease in oxygen solubility as shown in fig. 14, in which a straight line relation is obtained by plotting the characteristic rate of oxygen absorption against the oxygen solubility appropriate to the solution. The straight line passes through the origin.

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* The rate in N/5000 is identical with that in N/10,000, but the point has been unfortunately omitted from fig. 13.

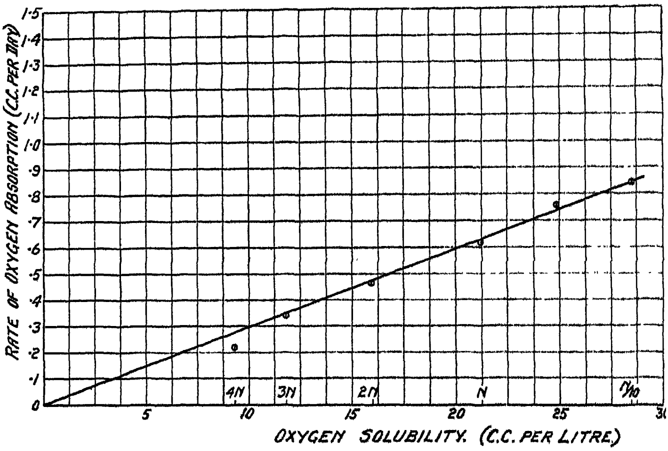

FIG. 14.—Rate of oxygen absorption—oxygen solubility.

It will be noticed that the ratio between the corrosion and the oxygen absorption rate is not constant over the whole range of concentration. The relatively high corrosion rate in conductivity water is due to the large percentage of ferrous iron in the corrosion product. The high corrosion rate in 4N KCl is due to a similar cause, together with a high proportion of corrosion due to hydrogen evolution.

The greater rate of corrosion which is obtained in N/10,000 KCl as compared with N/10 KCl is very remarkable and occurs, with all three materials used in the present research. In this respect, iron and steel are markedly different from zinc. However, the curves as given in fig. 11 do not give sufficient information about the relative corrosion rates during the first day. To investigate this, the following experiments were tried. Steel specimens were corroded for short periods up to 72 hours in the simple form of corrosion apparatus illustrated in fig. 1 of Part IV of this research,* with all the usual precautions. At the end of each period a specimen was removed from the thermostat and the corrosion products were brushed off and the iron in them estimated by the thiocyanate colour test. The results are given in Table IV, which show that corrosion actually starts up more quickly in the stronger solution, but dies down more rapidly, and at the end of 3 days the rate is less than in the weaker solution. The oxygen-absorption-time curve in N/10KCl is parabolic for the first two and a half days and then passes into a straight line. The explanation seems to be that the corrosion rate is determined by the rate at which oxygen reaches the metal surface, which is infinite initially but gradually falls as a gradient is established through the liquid.

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* 'Proc. Roy. Soc.,' A, vol. 131, p. 496 (1931).

Table IV.—Total Corrosion (in milligrammes).

Concentration.	6 hours.	12 hours.	18 hours.	48 hours.	72 hours.
N/10,000	2·6	4·6	6·8	13·4	17·2
N/10	4·6	6·8	8·3	13·4	15·0

Figs. 15 and 16 show that with increased oxygen supplies, steel in N/10 KCl may corrode faster than in N/10,000 KCl. Consequently the general shape of the curve shown in fig. 13 would be modified by higher rates of oxygen supply; that portion characteristic of the strong solutions might be raised well above the maximum value for the dilute solutions.

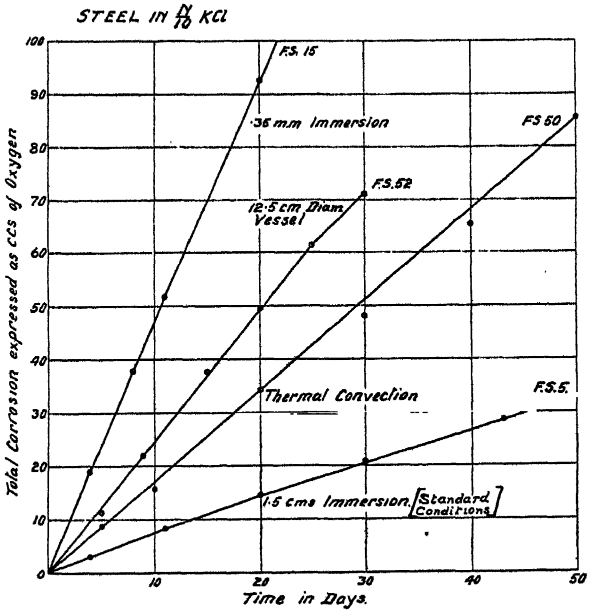

FIG. 15.—N/10 KCl—various oxygen supplies.

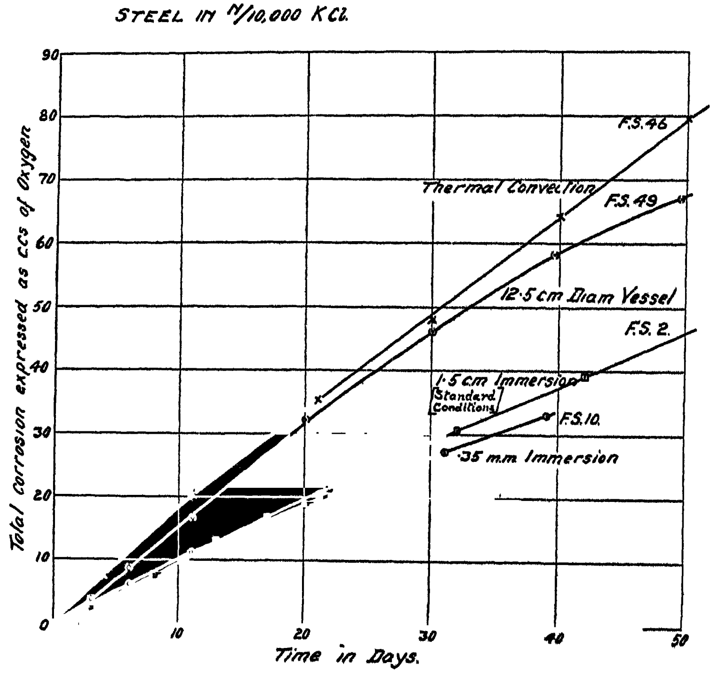

FIG. 16.—N/10,000 KCl—various oxygen supplies.

The Effect of Rate of Oxygen Supply to the Metal.

It has been suggested to the authors that their standard conditions are characterised by a very slow and uniform oxygen supply to the metal, which controls the rates of corrosion and so might mask effects which would be shown up by using larger supplies of oxygen.

Actually the corrosion rate in N/10 KCl in the authors' standard conditions is about 50 per cent. greater than that in an open beaker of similar size, notwithstanding that the Adeney effect assists the distribution of oxygen in the latter. The rate of oxygen supply can be further increased by three different methods, namely :—

(1) Increase of cross section of the vessel.
(2) Decrease of depth of immersion.
(3) The introduction of convection currents by means of temperature variations.

Under condition (3) the supply of oxygen will be no more uniform than in an ordinary experiment in an open beaker. All three methods have been used and rates of corrosion have been reached which are about 8 times as great as in the standard experiments and 12 times as great as those in a beaker of similar dimensions exposed to the air. In all cases the effect of the increased rates of oxygen supply was to give corrosion-time curves of similar form to those obtained in the standard conditions as shown in fig. 11, but with steeper slopes, as shown in fig. 15 which gives results in N/10 KCl; the fastest rate of corrosion is shown by specimen FS15 immersed at a depth of only 0·35 mm.; the next fastest is shown by FS52 in a vessel 12·5 cm. diameter; FS50 was placed in a standard vessel the bottom only of which was immersed in the thermostat at 25° C., while the top was exposed to the atmospheric temperature which was about 20° C.

Fig. 16 shows a similar set of results in N/10,000 KCl. In this solution the rate of corrosion in a vessel of diameter 12·5 cm. is less than that in N/10 KCl and is not increased by increasing the size of vessel to 15 cm. This shows that the shape of the curve in fig. 13 would be modified if higher rates of oxygen supply were used, the lower horizontal would be raised to, or even above, the higher. With thermal convection currents the rates in the two solutions are nearly the same; probably the movement of the liquid has a specific effect in the weak solution in addition to increasing the oxygen supply. Very shallow immersion also has a specific effect, because in both solutions the top surface of the specimen is almost completely free from attack, and in N/10,000 the rate of attack is not increased, whereas it is considerably in N/10. The fact that the corrosion rate is not increased in the dilute solution is further evidence that the process is not controlled by cathodic polarisation.

Other experiments have been carried out in the presence of convection currents. One was conducted in N/2 KCl in a standard apparatus placed on a laboratory bench instead of in a thermostat; others were carried out in open-bottom vessels of the standard apparatus in N/10,000 and N/10 KCl exposed to the open air. All gave straight-line curves nothwithstanding the gradual accumulation of corrosion products over the specimens. The rate in the standard vessel (see fig. 15, FS50) was nearly five times that in the open bottom vessel in a similar solution. These results show that the corrosion products do not act as oxygen screens even in the presence of ordinary convection currents set up by evaporation and variations of atmospheric temperature and pressure.

It is clear that in all these conditions in N/10 KCl the rates of oxygen absorption and corrosion are controlled by the rate of oxygen supply and that in nearly stagnant KCl solutions it is difficult or impossible to supply oxygen fast enough to escape this control, except perhaps by the use of pressures higher than atmospheric, such as are now being investigated. The nature and distribution of the corrosion products may also become an important factor in controlling corrosion rates in nearly neutral KCl solutions, but this factor will be discussed later in the section on micrographic work.

The Effect of Carbon Dioxide.

In the past, great importance has been attached to the effect of this gas; some authors considered it responsible for the actual initiation of corrosion, but Lambert and Thomson* showed that its presence was unnecessary to the process. Whitman, Russell and Altieri have shown that a decrease of p_H from 9 to 6 produced by carbon dioxide had practically no effect on the rate of corrosion in Cambridge (Mass.) water, and Speller considers that free carbon dioxide in the amount usually found in natural waters, is not *in itself* a factor of much importance. Steps are being taken to ascertain the effect of this gas on corrosion rates in pure KCl solutions, but the work is only in the initial stage. It has been found that in N/10,000 KCl the rate of corrosion during the first 50 days is the same in air purified by passage through potash as in ordinary laboratory air; during this period the corrosion-time curve is approximately a straight line. After 50 days the accumulation of mounds in purified air gradually cuts down the rate of corrosion; in laboratory air no mounds were found.

The Production of Hydrogen Gas.

Hydrogen gas is evolved from all three materials in all the solutions used. No bubbles, however, were observed adhering to the specimen or the corrosion products in any of the solutions, as was frequently the case with zinc. The measurement of the hydrogen was carried out by burning on a hot platinum wire.

Some typical curves are given in figs. 17 and 18. It will be seen that in weak solutions the hydrogen-time curves appear to be similar in form to the corresponding corrosion-time curves. In N/10 and stronger KCl solutions the curves are approximately straight lines passing through the origin. The initial rate of hydrogen evolution increases with concentration up to N/1000 KCl, after which it tends to become constant for all solutions as shown in fig. 19.

Much less hydrogen is evolved from the pure iron than from the standard steel when corroding in similar conditions. These hydrogen curves are quite

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* 'J. Chem. Soc.,' vol. 97, p. 2426 (1910).

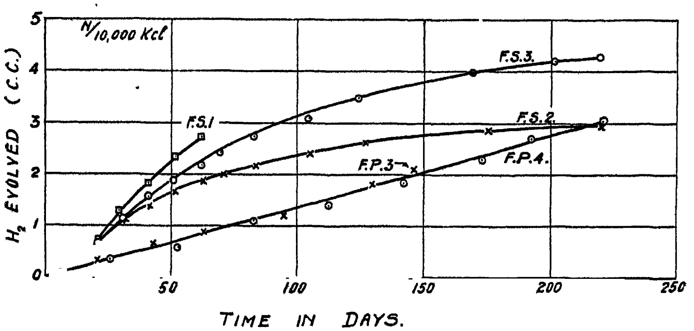

FIG. 17.—Hydrogen curves—N/10,000 KCl.

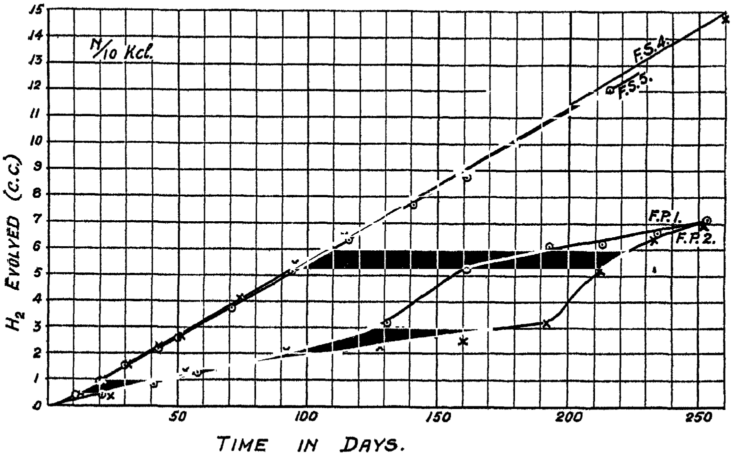

FIG. 18.—Hydrogen curves—N/10 KCl.

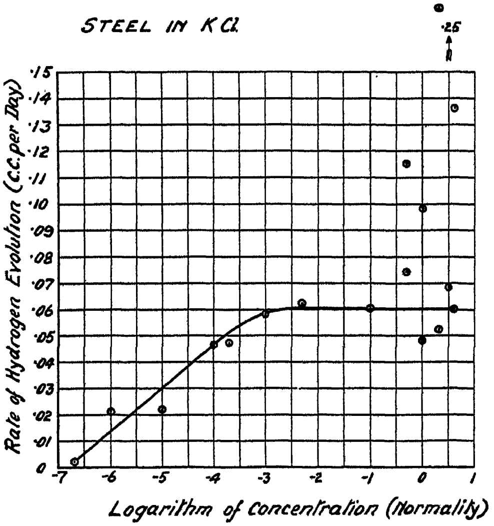

FIG. 19.—Hydrogen rate—conc. KCl.

different from the curves given in Part III* which were obtained with electrolytic zinc containing impurities of the order of 0·01 per cent. and which showed an acceleration in evolution rate due to the accumulation of insoluble impurities of lower overpotential than zinc. Iron itself has a low overpotential and steel contains a second phase in the form of carbide ; consequently there is no initial period of induction. The reproducibility of the hydrogen curves is often good, but sometimes rather sudden erratic changes occur, as shown in fig. 18. Notwithstanding the limits imposed by such occasional lack of reproducibility, two points come out clearly :—

1. There is a common rate of gas evolution from all solutions stronger than N/1000 (see fig. 19) although both the corrosion rate corresponding to the oxygen absorption process, and the oxygen solubility, are falling. These results are similar to those found for zinc, with which the final steady rate was the same for all solutions stronger than N/10. This suggests that the hydrogen gas process is independent of the oxygen absorption process and of oxygen solubility over the range considered. It may be further suggested that the hydrogen gas is not simply an excess which escapes oxidation, but that its rate of evolution is mainly determined by some other factor than oxygen supply. It will be noticed in fig. 19 that specimens in solutions of N/2 KCl and stronger usually show the hydrogen evolution rate of 0·06 c.c. per day, but some show a considerably higher rate. The reasons for the great variations in rates in this range are not known.

2. The similarity between the hydrogen time curves and the corrosion time curves for the weak solutions. A straight-line curve is obtained if the values for the total hydrogen evolution are plotted against the corresponding values for total oxygen absorbed. This suggests that a similar factor is at work controlling the corrosion corresponding to both sets of curves. Since hydrogen evolution appears to be independent of oxygen variations, it seems possible that anodic polarisation is playing an important part in determining the corrosion in these solutions, as already suggested for other reasons.

The proportion of the total corrosion due to the evolution of hydrogen gas is given in Table V. Occasionally, values exceeding anything found with zinc have been observed, such as 45·5 per cent. in 3N KCl.

Schikorr† has suggested that the hydrogen gas evolved when iron corrodes is due to a reaction between ferrous hydroxide and water, rather than between iron and water. In the authors' opinion there are serious objections to this

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* 'Proc. Roy. Soc.,' A, vol. 127, p. 63 (1930).

† 'Z. Elektrochem.,' vol. 35, p. 65 (1929).

Table V.

Solution.	Conductivity water.	N/1,000,000.	N/100,000.	N/10,000.	N/1000.	N/200.
Per cent. of corrosion due to hydrogen gas after 100 days	Trace	1·3	1·1 2·0	2·2 1·8	3·9 4·8	4·1 5·5

Solution.	N/10.	N/2.	N.	2N.	3N.	4N.
Per cent. of corrosion due to hydrogen gas after 100 days	5·0 4·7	7·1 11·1	9·6 11·1	26·7 17·4	12·2 45·4	16·7 32·4

view. For instance, Schikorr never obtained any hydrogen gas from iron oxides in the presence of water unless metallic iron was present; moreover, it is known that iron does displace small amounts of hydrogen gas from water in the absence of oxygen and iron oxides. Moreover, although ferrous oxide is being produced more rapidly in N/10,000 KCl than in N/10, the rate of hydrogen evolution is much less.

A comparison between the hydrogen evolution from steel and zinc suggests that the process is fundamentally the same for both metals. It was shown for zinc that hydrogen was evolved from the corroded areas, but this has not yet been verified for iron, because of the smaller amount of gas evolved.

Comparison of the Corrosion Curves for Zinc and Iron.

A comparison of a few curves for iron with those for zinc obtained under similar experimental conditions, shown in fig. 20, reveals some remarkable facts. A few of these are as follows :—

1. Both iron and steel corrode at much faster rates, and maintain their rates for considerably longer periods, than zinc in conductivity water and dilute solutions up to N/1000 KCl. In conductivity water the total corrosion as oxygen for standard steel FS12 after 25 days was 4·1 c.c.; that for a zinc specimen after 25 days was 0·125 c.c. This difference is probably due to the different physical properties of the respective hydroxides of the two metals, but not to their respective solubilities; a saturated solution of ferrous hydroxide contains 3·8 parts of iron in a million, and a similar solution of zinc hydroxide contains 3 parts of zinc in a million, a difference far too small to account for

the difference in total corrosion. The difference between the two metals in the weak chloride solutions is chiefly due to the removal of the chloride ion from solution, which occurs during the corrosion of zinc, but not with iron and steel.

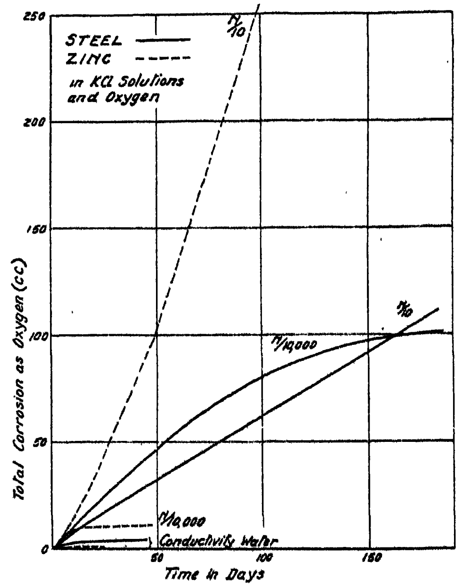

Fig. 20.—Comparison Zn and Fe curves.

2. In N/10 KCl, all three materials used in this research corrode at slower rates than zinc for considerable periods of time. Since, however, the corrosion rate of zinc falls to a very small value at about 120 days, whilst that of iron continues up to at least 500 days, the corrosion-time curves cross and the iron after long times gives a greater total corrosion.

3. In all solutions stronger than N/10 the standard steel corrodes at slower rates than zinc and maintains a characteristic rate for very long periods.

4. The maximum rate of oxygen absorption for iron in the standard conditions occurs in N/10,000 KCl, whereas for zinc the maximum is between N/50 and N/10. The values of these maxima are the same and are determined by the dimensions of the corrosion vessel. With increased rates of oxygen supply the rate of corrosion of iron is increased more in N/10 than in N/10,000.

5. The rate of oxygen absorption in N/10 KCl for iron during the first 4 days at shallow immersion of 0·35 mm. is 6·5 c.c. per day as compared with 8·5 c.c. for zinc; at the standard depth of 15 mm. the oxygen absorptions are 0·84 c.c. for iron and 1·45 c.c. for zinc.

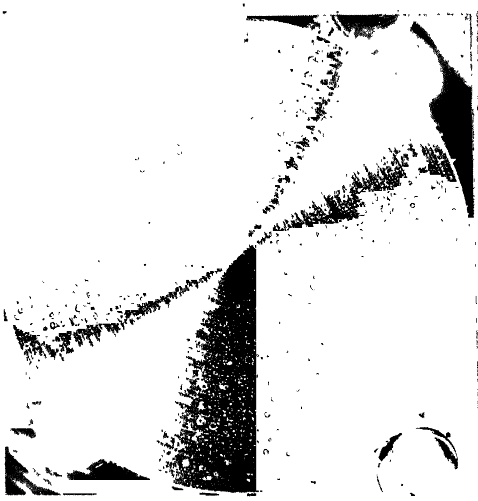

Fig. 21.—7 minutes.

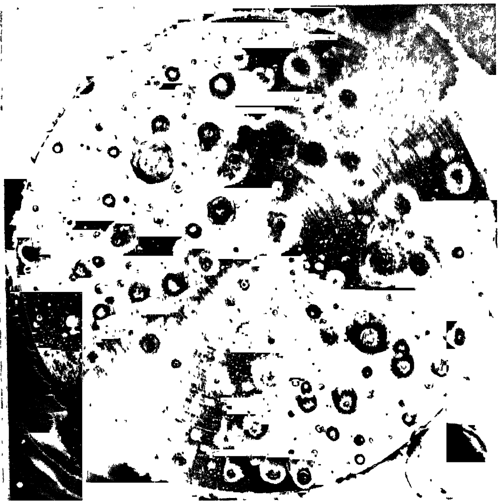

Fig. 22.—2½ hours.

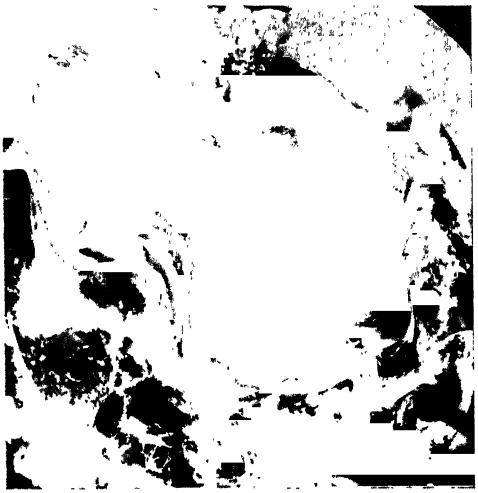

Fig. 23.—37 days.

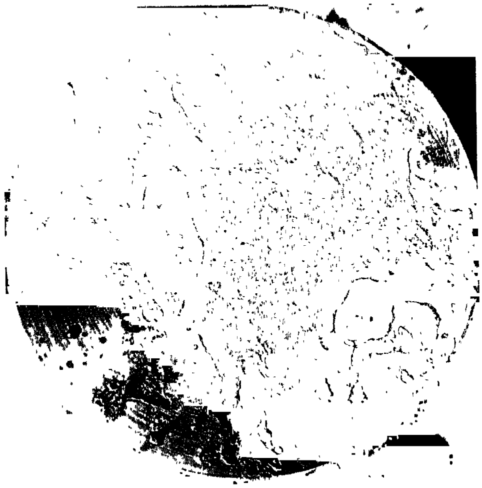

Fig. 24.—37 days. Corrosion product removed.

Steel in N/100,000 KCl and Oxygen (× 2½).

FIG. 25.—Pure Iron turned (× 24). After 5 minutes in N/10,000 KCl. 1,200 centres per sq. cm.

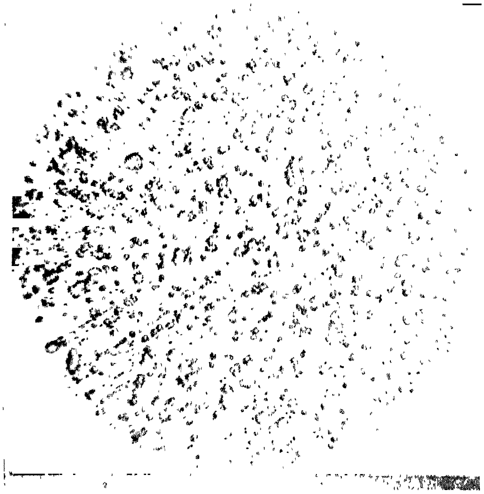

FIG. 26.—Steel turned (× 24). After 2½ minutes in N/10,000 KCl. 12,000 centres per sq. cm.

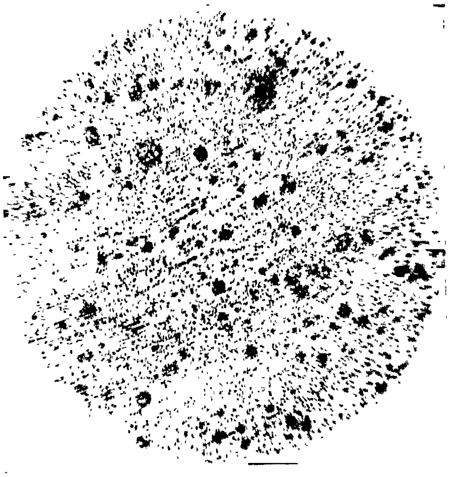

FIG. 27.—Steel turned and heated to 185° C. (× 24). After 2½ minutes in N/10,000 2,000 centres per sq. cm.

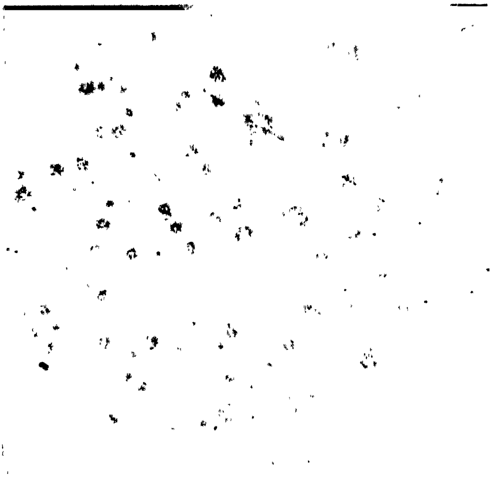

FIG. 28.—Steel emery polished 0000 H. (× 24). After 2½ minutes in N/10,000 KCl. 2,500 centres per sq. cm.

6. The differences in the oxygen-corrosion rate between zinc and iron over the whole range of solutions studied are due to the different properties of the respective corrosion products, and not to the differences in the basic values of the (unpolarised) e.m.f. as stated by Evans.*

The Mechanism of Corrosion of Iron and Mild Steel.

Micrographic observations on the progress of corrosion have been made in the apparatus described in Part IV of this research.† The pure iron and standard steel were used in N/100,000, N/10,000 and N/10 KCl. 350 c.c. of solution were used, otherwise the conditions were similar to the standard experiments except for temperature fluctuations over a range of 21 ± 2°.

Experiments in N/100,000 KCl *on Turned Specimens of Standard Steel.*

Corrosion started at a large number of sporadically distributed centres, about 1500 per square centimetre as estimated at the end of 2·5 minutes. Fig. 21 (Plate 4) shows the state of affairs at the end of 7 minutes, and figs. 22 and 23 at the end of 2·5 hours and 37 days. Fig. 24 shows the specimen with corrosion products removed after 37 days' corrosion. Fig. 22 shows that corrosion is only maintained at a limited number of centres and that even at the end of 2·5 hours the majority of the original corrosion centres have already ceased to operate, notwithstanding the presence over them of deposits of corrosion product which are usually considered to behave as oxygen screens and to maintain corrosion. Fig. 23 shows the larger secondary mounds of corrosion product beneath which most of the corrosion was concentrated as shown by comparison with fig. 24. The impervious walls of the secondary mounds are shown light in the figure. Within the walls there are loose ferric and black magnetic oxides, through which oxygen can penetrate to the metal.

Experiments in N/10,000 KCl.—Similar phenomena were found in this solution. Corrosion began on turned standard steel at a large and variable number of centres which might be as many as 10,000 per square centimetre as counted at the end of 2·5 minutes. On purified iron the number was reduced to about 1200 per square centimetre. Heating a turned standard specimen to about 185° C., for half-an-hour, which gives the oxide film stated by Evans‡ to be the most protective, reduced the number of centres to about 2000. A specimen polished on emery paper (0000 Hubert) and degreased in benzene showed about 2500 centres. These facts are illustrated in figs. 25 to 28 (Plate 5).

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* U. R. Evans, 'J. Chem. Soc.,' p. 125 (1929).

† 'Proc. Roy. Soc.,' A, vol. 131, p. 507 (1931).

‡ U. R. Evans, ' J. Chem. Soc.,' p. 1028 (1927).

The initial distribution of corrosion just described seems to be determined largely by the situation of the most reactive atoms in the metal surface, and by the configuration of the surface itself. For instance, tears, burrs and edges of surfaces give rise to preferential attack, probably owing to ease of access of the reactants and failure to form a precipitated protective film over sharp edges.

This initial, nearly sporadic, distribution of corrosion undergoes a series of changes which results in the aggregation of the attacked and relatively unattacked areas into a few large distinct patches as shown in figs. 21 to 24. The stoppage of corrosion at many centres seems to be due to the direct precipitation over them of a protective film of ferric hydroxide, which mainly dictates the final distribution of corrosion. The gradual building up of mounds over the attacked areas determines the rate of corrosion.

It was noticeable that, though the number of starting centres was much less on purified iron than on steel, the ultimate distribution of corroded areas was similar to that on the standard steel. The corrosion rate of the iron was only slightly less than that of the steel and this was partly due to the lower rate of hydrogen evolution and partly to the different behaviour of the hollow mounds of corrosion products which were gradually built up. The corroded areas were always located beneath the large mounds, the bright protected areas were outside them.

In the early stages of these experiments the hollow mounds had open mouths, similar to those shown in fig. 23, through which oxygen could readily penetrate to the metal surface, but these openings gradually contracted till they were finally almost closed. In parallel experiments in the thermostat a decrease of corrosion rate was found to accompany the contraction. The relatively bright areas outside the mounds remained practically constant during the whole corrosion process. They generally constituted about 50 per cent. of the whole area of the specimen.

The mounds on the under surface of the specimens often had tubular deposits of oxide hanging loosely from them. The removal of these loose deposits had no effect upon the corrosion rate, which was controlled mainly by the behaviour of the denser mounds such as that shown in fig. 23.

The usual view that the distribution of corrosion over the surface of the metal is determined by the presence of " weak points " in an otherwise protective air-formed film does not agree with the facts recorded above because :—

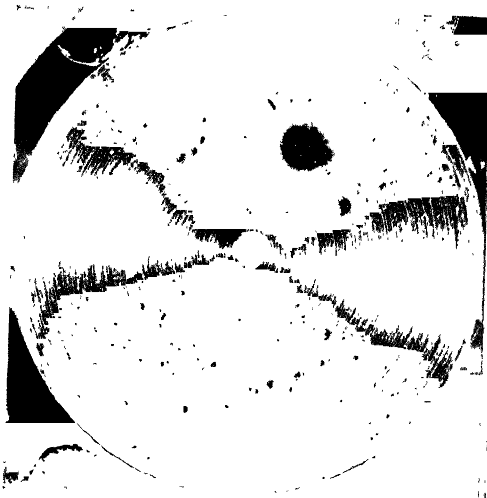

Fig. 29.—9 minutes.

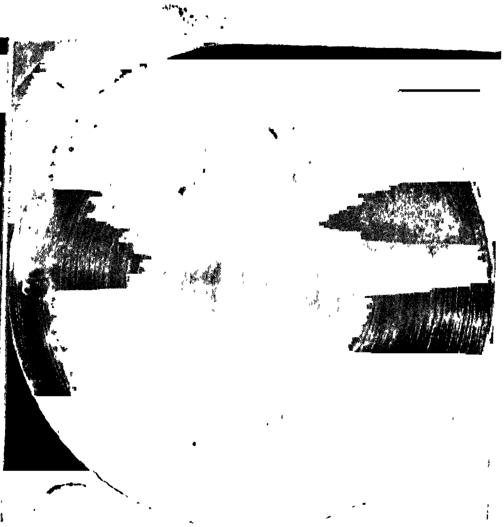

Fig. 30.—50 minutes.

Fig. 31.—1 day.

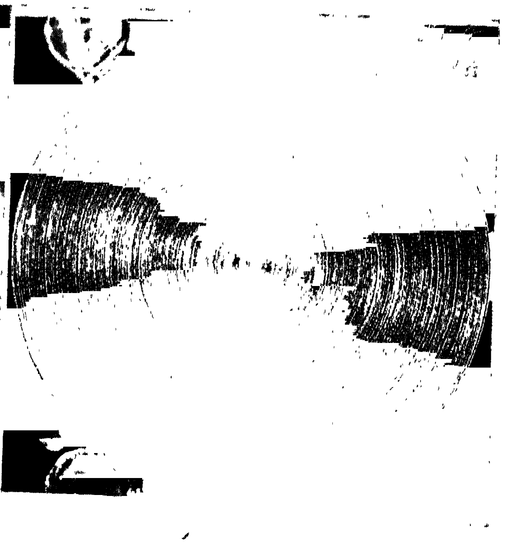

Fig. 32.—1 day. Corrosion product removed.

Steel in N/10 KCl and Oxygen (× $2\frac{1}{2}$).

1. The final distribution of corrosion is quite different from the initial distribution, whereas on the air-formed film and differential aeration theories, " a ring of rust is formed at an appreciable distance from the point of origin, and such rust is not protective (it actually stimulates attack by screening from oxygen)."* Consequently, on this theory every centre of corrosion which has once started and produced visible rust, such as those shown in figs. 21 and 26, should continue to operate, whereas the experimental fact is that the majority of them cease to function.
2. The fact that corrosion usually begins at several thousand centres per square centimetre suggests that the ordinary air-formed film can hardly be called protective in chloride solutions, even when saturated with oxygen which is stated to repair the film.†

Experiments in N/10 KCl.—Figs. 29 to 31 (Plate 6) show the top surface of a specimen at the end of 9 minutes, 50 minutes, and 1 day. Fig. 32 (Plate 6) shows the metal surface cleared of corrosion products at the end of the experiment. The whole surface of the metal is corroded except that portion within the crescent-shaped ridge of fig. 36. Corrosion appears to start very rapidly at fewer centres than in weaker solutions, and spreads much more rapidly (the light areas in the photos are corrosion products covering corroded areas). In this solution a rapid change in distribution takes place in the first few hours, whereas in the weak solution a corresponding change occupies several days.

The initial attack again takes place at tears and burrs on the ridges of turning marks and the attack is so rapid‡ that the concentration of alkali produced over other parts of the specimen probably prevents or retards the development of corrosion at other centres which could develop in weak solutions. This alkali can be detected by indicators near both the top and bottom surfaces of the metal during the first few minutes of the attack. It soon disappears from the top surface, no doubt owing to interaction with ferrous ions, but remains on the bottom where the attack does not develop.

In both N/10 and stronger KCl solutions the bottom surface of a specimen was always less corroded than the top during the intermediate periods of the experiments. After long periods the whole of the top, bottom and sides of the specimens were attacked in N/2 and stronger solutions ; in N/10 solution the uncorroded part, which was on the bottom, was reduced to 26 per cent. of the whole in the longest experiment tried (268 days). To throw light on the cause of the temporary protection of the bottom surfaces an experiment was tried with N/10 KCl in the apparatus illustrated in fig. 23 of Part IV of this research. This apparatus admits oxygen first to the bottom surface of the specimen and so separates out this effect from gravity. It was found that the bottom surface was again relatively protected ; consequently gravity seems to play a part in the protection. Some of the ferric hydroxide produced by the corrosion process is in such a fine state of division that it has been observed to rise into the liquid above the top surface of a specimen and sometimes adheres as a thin transparent film to the walls of the vessel. It is probably a film of similar material, which cannot rise and therefore sticks to the bottom surface, which retards the solution of the metal. Any films formed in strong solutions would cause local accumulation of excess alkali which would assist in retarding solution of metal.

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* U. R. Evans, Bannister and Britton, 'Proc. Roy. Soc.,' A, vol. 131, p. 372 (1931).

† *Ibid*, p. 356; U. R. Evans, 'J. Chem. Soc.,' p. 123 (1929); U. R. Evans and S. C. Britton, " First Report of the Corrosion Committee to the Iron and Steel Industrial Research Council," p. 145 (1931).

‡ See Table IV on p. 325.

Conclusions.

From the joint results of the micrographic and corrosion velocity work some important conclusions emerge :—

1. The initial air-formed film of oxide which is present on all ordinary specimens of iron and steel that have been exposed to the atmosphere has little or no effect on the amount or final distribution of corrosion. No difference could be detected in the behaviour of specimens that had been exposed to dry air for 1 hour or 4 weeks, and subsequently corroded in either conductivity water or N KCl. The air-formed film is so easily penetrated at vast numbers of points, even in highly dilute chloride solutions, that its protective effect is negligible.
2. Areas temporarily or permanently free from corrosion in chloride solutions are covered with a precipitated protective film formed by the corrosion process itself. This appears to consist of a special transparent form of ferric hydroxide, which may originate either close to the metal surface or in the body of the liquid, adhering subsequently to the metal. It differs from the ordinary flocculent form of ferric hydroxide in being highly insoluble in dilute acids and almost impermeable to oxygen and ions. A film of this material " blankets " many of the initial centres of corrosion.

3. In N/2 and stronger KCl solutions the protection afforded by the film is only temporary owing to undercutting. Consequently in long-continued experiments the whole surface of the metal is attacked. No protective current density, as postulated by U. R. Evans,* is ever reached at the temporarily protected film-covered areas.
4. Neither the loose gelatinous ferric hydroxide nor the stable black magnetic oxide which constitute the bulk of the "rust" formed beneath atmospheres of oxygen and air have any important retarding action on the access of oxygen to the metal in N/10 and stronger KCl solutions; they do not, therefore, act as effective oxygen screens as assumed by the great majority of corrosion workers.
5. The particular form of corrosion product which gradually builds up as mounds in very dilute solutions in the presence of oxygen does act as an oxygen screen and greatly cuts down the rate of corrosion; the presence of carbon dioxide prevents the formation of the screen.
6. Considerable changes of distribution of the attacked and unattacked areas take place, and at no stage of the corrosion process can the anodic areas be precisely identified, since some depolarisation takes place at corroded areas. In the later stages of corrosion in strong solutions no definite cathodic areas can be identified and even in the early stages the apparently cathodic areas are not the sole cathodes.†
7. There is no reason to suppose that any differential aeration that may occur over the surface of horizontally arranged totally immersed specimens at moderate depths exercises any important effects on either the velocity or distribution of corrosion.
8. In dilute solutions the velocity of corrosion is generally determined by the rate of oxygen supply to the corroded areas of the metal surface, although the whole of the metal surface is available for cathodic depolarisation.‡
9. The distribution of corrosion is determined by the nature and distribution of precipitated corrosion products which locally protect the metal by mechanically obstructing the entrance of ions into solution.

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* 'Proc. Roy. Soc.' A, vol. 131, p. 355 (1931).

† *Cf.* Whitman and Russell, 'Ind. & Eng. Chem.,' vol. 16, p. 276 (1924).

‡ *Cf.* Wilson, 'Ind. & Eng. Chem.,' vol. 15, p. 127 (1923).

10. Hydrogen gas was evolved in all the solutions tested. The proportion of the total corrosion due to gas evolution became important in all solutions stronger than about N/1000 KCl, and, exceptionally, rose as high as 45 per cent. in 3N, a figure never reached with zinc.

These conclusions are based on experiments carried out in a range of conditions from extreme stagnancy to those in which convection currents, such as occur in open beakers, were present.

It is clear that some of these conclusions differ from those reached by U. R. Evans, Bannister and Britton.* These authors consider that the distribution of corrosion on zinc and iron is largely determined by the distribution of aerated and relatively unaerated parts of the metal, and that its amount is proportional to the current flowing between the two. They believe that this current can be "tapped" and shown to correspond closely to the actual corrosion that accompanies it. They consider that normally this corrosion rate is controlled by cathodic polarisation which is due to limitation in the rate of oxygen supply; also that a definitely protective current density is reached at cathodic areas on electrolytic iron and steel; this results from the spreading or contraction of the anodic areas till a certain balance between the two is reached.

The present authors agree that polarisation usually occurs at cathodes and may limit the rate of corrosion (this is what happens with zinc† in all the experiments they have described as being under oxygen control), but they dissent from all the other conclusions. The reason for the different conclusions reached is no doubt to be found in the different experimental methods used. Evans, Bannister and Britton have made measurements in three sets of conditions, namely:—

1. Loss of weight and current measurements with an iron anode shielded from oxygen by a cellulose acetate screen and paraffin, and an iron cathode round which oxygen was bubbled.
2. Potential measurements on pairs of different metals such as zinc and copper, and on different parts of partially immersed iron.
3. Current density and potential measurements on an iron cathode with a platinum anode. An external e.m.f. was used.

All the experiments were done with half-immersed specimens, but their conclusions are stated in general terms and are apparently intended to apply to completely immersed specimens also. These conclusions are, therefore, based on an assumed analogy between their experiments and the conditions that occur at the surface of an ordinary completely immersed corroding specimen of metal.

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* 'Proc. Roy. Soc.,' A, vol. 131, p. 355 (1931).

† 'Proc. Roy. Soc.,' A, vol. 116, p. 466 (1927); and vol. 121, p. 97 (1928).

The fact that the present authors' experiments point to different conclusions suggests that the assumed analogy does not hold, probably for the following reasons :—

1. Nothing at all analogous to the cellulose acetate screen and rapid cathodic aeration can occur at the surfaces of zinc and iron completely immersed in stagnant liquid ; the present authors have shown that the masses of corrosion products on zinc and iron do not behave as oxygen screens, except in very dilute solutions on iron ; in these exceptional conditions they cut down the rate of corrosion instead of stimulating it.
2. The general process of corrosion is greatly modified by the use of two different and separated metals instead of a single piece of metal, since the distribution and effects of both alkali and corrosion products will be quite different.
3. The assumption is incorrect that anodic processes are of such minor importance that an entirely different metal can be substituted without affecting the process. In the cathodic potential experiments described in 3 above, there is no product entering the solution from the platinum anode and consequently no removal of the cathodic alkali by precipitation such as occurs in an ordinary corrosion experiment.

   Moreover, Evans, Bannister and Britton produce no evidence to show that the protective current density given in their paper is that which occurs over the protected areas of specimens actually corroded in similar conditions of oxygen supply.

In view of the complicated conditions occurring over the surface of a corroding metal it must always be difficult to devise a series of experiments in which each electrode process can be isolated and studied separately without interfering with the essential nature of the corrosion process itself. Consequently any conclusions reached from such experiments will be subject to limitations which cannot be closely defined. The essential basis for the study of the velocity and mechanism of corrosion is a large collection of accurate quantitative measurements on metals corroding under a variety of defined and reproducible external conditions in each of which the controlling factor has been ascertained.

The authors wish to acknowledge the help they have received in the experimental work from Mr. T. J. Nurse. The research was carried out for the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research, and the thanks of the authors are due to the Chairman, Professor Sir Harold Carpenter and to Professor G. T. Morgan for many facilities afforded and for permission to publish.

APPENDIX I.

Manufacture of Standard Steel.

A specially promising ingot was selected from those that passed through the tube department of the Vickers Works. Its cross-section was 17 inches by 15 inches and it had been cast from an acid open-hearth furnace. It was rolled into billets and rough-turned to 6 inches diameter. From the billets discs were cut at both ends and examined by sulphur-printing for blow-holes. A selected billet was machined down three-eights of an inch and its surface ground all over and again examined for blow-hole segregation. Since one segregate remained, another eighth of an inch was machined off all round. A careful macro-examination was then made, before and after etching in 10 per cent. nitric acid, for visible slag inclusions and structural variations. Since these were absent, the machined billet, now 5½ inches in diameter, was cogged down to 2 inches square and sawn into three pieces, one of which was rolled directly into a round bar, 1¼ inches in diameter. The other two pieces were reheated and rolled to the same diameter, the finishing temperatures being 770°, 760° and 750°.

Two of these bars were then reeled and all three were subsequently heated to 840° and slowly cooled in the furnace. The split ends were cut off and cross-sections were submitted to macro-examination by sulphur-printing and nitric acid etching. These showed the bars to be sound and no structural variation or slag inclusions could be seen. Micro-examination showed slight differences in the structure between the two ends of the bars which were between 8 and 9 feet long. These variations were probably due to temperature differences during annealing; consequently, the bars were cut into lengths of 2½ feet and carefully heated with special precautions. They were supported on knife edges carried on a base plate and placed in a gas-heated furnace at a temperature of 500°. The furnace door was looted up and the temperature raised to 900–920° in 2½ hours. The temperature was held at 905–995° for ½ hour and the base plate and the bars were then taken out and cooled to atmospheric temperature in the absence of draughts, in a cold furnace with doors open but dampers closed. Transverse sections were cut from the ends of each bar and examined microscopically. They were closely similar to one another, and fig. 3 is a typical photomicrograph; it shows white ferrite with dark sorbite areas at the junction of the ferrite crystals. The analysis of the steel is given in Table I.

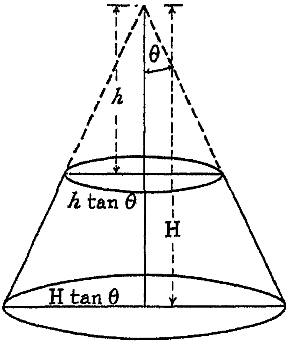
The whole of the work on the production of this steel was arranged and supervised by Mr. W. H. S. Dickenson, to whom the authors wish to express their gratitude.

APPENDIX II.

The Effect of Corrosion Mounds on Corrosion Rate.

Case 1.—The mounds build up in the form of hollow cones.

Suppose the corrosion product is building up from the base so as to form a cone as in the figure, of angle 2θ and height H, and that at a time t the height reached is $H - h$.



Then, area of opening of truncated cone $= \pi h^2 \tan^2 \theta$,

and area of curved surface of truncated cone $= \dfrac{\pi \sin \theta}{\cos^2 \theta} (H^2 - h^2)$.

Let the total corrosion at time t be y and assume that

$$y \propto \frac{\pi \sin \theta}{\cos^2 \theta} (H^2 - h^2), \tag{1}$$

and that the rate of corrosion is proportional to the opening, *i.e.*,

$$\frac{dy}{dt} \propto \pi \tan^2 \theta \,.\, h^2. \tag{2}$$

Substituting for h^2 from (1), (2) may be written

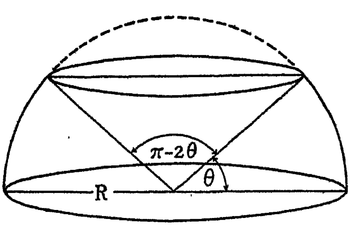
$$dy/dt = k(a - y)$$

whence

$$y = A(1 - e^{-kt}).$$

Note.—If the mounds build up in the form of flat circular areas, a similar result will be obtained.

Case 2.—The mounds build up in the form of hollow hemispheres. Suppose the corrosion product is building up from the base to form a hemisphere of



radius R as in the figure, and that at a time t the opening subtends an angle $\pi - 2\theta$ at the centre of the base. Then the area of the circle opening

$$= \pi R^2 \cos^2 \theta,$$

and the area of the curved surface

$$= 2\pi R^2 \sin \theta.$$

Now let the total corrosion at time t be y and assume that

$$y \propto 2\pi R^2 \sin \theta, \qquad (1)$$

and that the rate of corrosion is proportional to the opening, *i.e.*,

$$\frac{dy}{dt} \propto \pi R^2 \cos^2 \theta \qquad (2)$$

from (1) $\sin \theta = k_1 y$, and (2) may be written $dy/dt = k_2 (1 - \sin^2 \theta)$

from (1) and (2) $dy/dt = a - by^2$,

whence $y = k \tanh ct$.

Summary.

The oxygen absorption method of measuring corrosion which was developed for zinc has now been adapted for iron and steel. Two types of corrosion time curves have been obtained in KCl solutions, namely, exponential for weak and linear for strong solutions; each is associated with a characteristic type of corrosion product. Hydrogen gas was evolved in all solutions and the proportion of the total corrosion due to this type of action was considerable in all solutions stronger than N/1000; the general shapes of the hydrogen evolution time curves were similar to those for the corresponding oxygen-absorption curves.

Micrographic observations were made to supplement the corrosion velocity measurements. The results showed that the characteristic distribution of corrosion over completely immersed horizontal specimens was determined neither by the initial air-formed film nor by any differential aeration that could occur in stagnant solutions, but mainly by the distribution of a particular form of precipitated corrosion product. The deposits of rust which are usually supposed to behave as oxygen screens and stimulate corrosion by differential aeration do not so behave in any solution stronger than N/1000 KCl; the rust was found to consist almost entirely of mixtures of ferric oxide and stable magnetic oxide. In very weak solutions in the presence of oxygen the rust was usually built up into coherent mounds which did act as oxygen screens but gradually reduced corrosion rates.

Highly purified iron gave nearly the same rate of corrosion as mild steel in N/10 KCl, but the rate of evolution of hydrogen gas was less. In conductivity water both purified iron and steel corroded at much higher rates than zinc, but in N/10 KCl much more slowly. The main causes of these differences are to be found in the different properties of the corrosion products.

The Effect of Frequency on the Condensed Discharge Ignition of Carbonic Oxide-Air Detonating Gas.

By G. I. Finch and H. H. Thompson, Imperial College of Science and Technology, London.

(Communicated by W. A. Bone, F.R.S.—Received June 24, 1931.)

Introduction.

The thermal theory of the mechanism of the ignition of an explosive gaseous mixture by an electric discharge was put forward by Taylor-Jones, Morgan and Wheeler,* in terms stating that " the ignition of a gaseous mixture depends primarily . . . on the heating of a sufficient volume to a sufficient temperature."

The electrical ignition of gases has been studied by R. V. Wheeler,† Taylor-Jones,‡ Holm,§ and J. D. Morgan,‖ all of whom have put forward facts purporting to establish a purely thermal theory which, it is claimed, explains the mechanism of ignition as a whole, whether by electric discharges or by any other means.

We have never been able to subscribe to this view, for reasons which are briefly as follows. The thermal theory necessarily implies either that the sole means of increasing internal molecular energy is by an increase in translatory energy, or that internal molecular energy plays no rôle in ignition, or, indeed, in combustion. Now, since it cannot be supposed that the mean internal energy of the molecules of a volume of gas can only be increased by increasing their mean kinetic energy, the thermal theory necessarily involves the supposition that ignition is primarily determined by the translatory energy of the molecules, and not by their activation.

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* 'Phil. Mag.,' vol. 43, p. 359 (1922); see also "Safety in Mines Research Board," Paper No. 11, Mines Department (1925).

† 'J. Chem. Soc.,' vol. 127, p. 14 (1925).

‡ 'Phil. Mag.,' vol. 6, p. 1090 (1928).

§ 'Phil. Mag.,' vol. 11, p. 194 (1931).

‖ 'Phil. Mag.,' vol. 45, p. 968 (1923); vol. 49, p. 323 (1925); vol. 11, p. 158 (1931).

There are, however, many well-established facts which appear to contradict any such conclusion. Thus, for example, might be cited (1) the well-known phenomenon of the photo-ignition of hydrogen-chlorine mixtures; (2) H. B. Dixon and Croft's* experiments on the ignition of hydrogen-oxygen mixtures by adiabatic compression, which showed that dilution with oxygen in excess of the equivalent amount reduced the temperature of ignition; (3) the abrupt nature of the setting up of positive column combustion in electrolytic gas, noted by Finch and Cowen†; and (4) the facts established by Hinshelwood and his co-workers‡ in their recent studies on the combination of hydrogen and oxygen.

In contradistinction to the thermal theory, the electrical theory of ignition implies that the ignition of an explosive gaseous mixture is determined by the setting up of a sufficient concentration of suitably activated§ molecules of the constituent gases. It will be noted that, whereas the rôle played by the translatory energy of the molecules is fundamental to the thermal theory, the electrical hypothesis disregards such kinetic energy, except in so far as it is one, but only one, of several possible influences which may contribute to the formation of suitably activated molecules and lead to their approach to each other. Up to the present time, however, no direct experimental evidence has been available which would enable a definite decision to be made between the two views in question.

We now propose to describe experiments on the ignition of equivalent mixtures of carbonic oxide and air by means of condenser discharges—primarily undertaken in connection with a study of ignition by induction coil discharges now being carried out in these laboratories—the results of which render untenable the thermal theory of ignition, because they show that discharge oscillation frequency is a far more potent factor in determining ignition than either the rate or amount of energy dissipation in the discharge.

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* "Flame and Combustion in Gases," by W. A. Bone and D. T. A. Townend, p. 75, (Longmans Green & Co., 1927).

† 'Proc. Roy. Soc.,' A, vol. 111, p. 257 (1926).

‡ Summarised in 'Proc. Roy. Soc.,' A, vol. 130, p. 640 (1931).

§ By "activation" is meant here any increase in the internal energy of a molecule; quantised when the molecule as such remains intact, but generally unquantised when ionisation or atomisation occurs.

EXPERIMENTAL.

General Conditions.—Mixtures of carbonic oxide and air in their equivalent proportions were ignited by means of condensed electric discharges of known oscillation frequency. The igniting power of the spark was determined in terms of the ignitibility of the mixture as measured by the lowest pressure at which ignition was just able to occur. The conditions were so arranged that the effect of frequency upon igniting power could be studied independently of either the amount or rate of energy dissipation occurring either in the first half cycle or in the complete discharge.

The Apparatus.—The volume of the explosion vessel, fig. 1, was approximately 80 c.c. One electrode was sealed in with sealing wax; the other formed a sliding fit in its side-tube, a flexible gas-tight joint being made in the manner shown by means of thick-walled rubber tubing. The gap width could be reduced by pressure on the insulated handle of the movable electrode. Aluminium electrodes of 5 mm. diameter, with the spark-gap ends rounded off into hemispheres were employed. Aluminium was chosen for this purpose, because its cathode potential fall is low, and on account of its comparative freedom from cathodic sputtering.

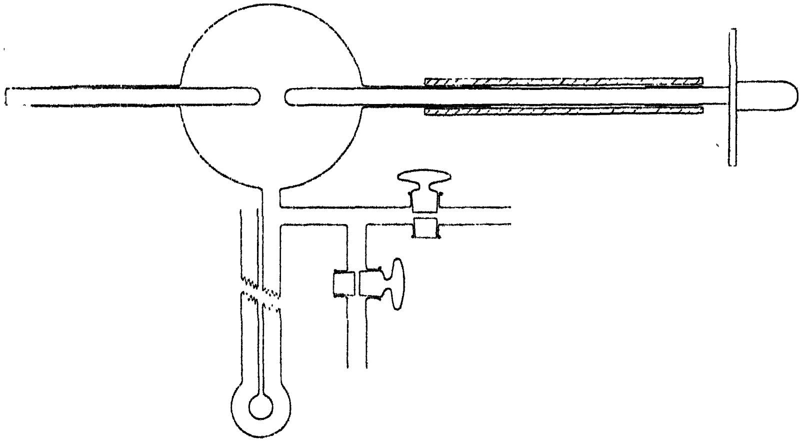

FIG. 1.—Explosion vessel.

The electrical circuit, fig. 2, consisted of a high-tension transformer and a Mullard VU 7 diode, by means of which the condenser, C, could be charged through the high-frequency chokes, l_1 and l_2, to a known pressure, as measured on the electrostatic voltmeter, V. The capacity of this instrument formed a negligible addition to that of C. C could be discharged through the inductance,

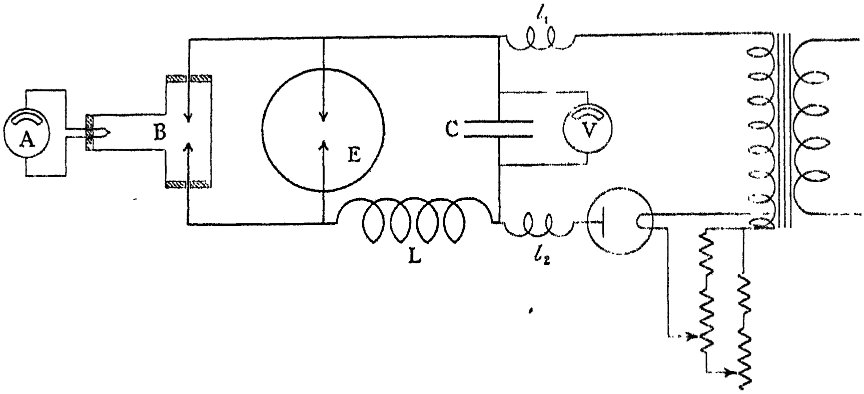

FIG. 2.—Electrical circuit.

L, across either the spark gap in the explosion vessel, E, or that in the vessel B, which contained a silver-constantan thermocouple connected to the microammeter, A. One electrode was adjustable in the vessel, B, and could be clamped in any desired position. This vessel was enclosed in a box loosely packed with cotton-wool.

The oscillation circuit, indicated by the heavily drawn lines in fig. 2, consisted, apart from the plates of the condenser and the electrodes, either of copper tubing of 5 mm. external and 1·5 mm. internal diameter, or of conductors approximately equivalent thereto, and was laid out as compactly as was practicable. Junctions were either heavily soldered or made by firmly clamping together large, well-fitting and cleaned areas.

The following condensers were available and were employed for the purpose of these experiments :—

(i) A bank of low resistance, mica dielectric condensers of low inductance and provided with tappings at 0·041, 0·051, 0·066 and 0·071 μF.

(ii) Two oil-immersed paper dielectric condensers of 0·2 μF each. These were of Mansbridge pattern; their resistance and inductance were therefore proportionately much greater than those of the mica pattern in which the alternate layers of small rectangular and comparatively heavy gauge sheet tin conductors were soldered throughout the length of a longer side to their respective common bus-bars.

The inductance, L, was built up as required out of 2-turn coils of copper tubing of 1·5 mm. bore and 5 mm. external diameter. The coil diameter and spacing were 7·5 and 1·5 cm. respectively. The frequency of the discharge circuit was measured by means of an absorption wave meter.

Procedure.—After alternate evacuation and flushing out, the explosion vessel was filled to a known pressure with a mixture of carbonic oxide and air in their equivalent proportions, previously dried by passage through a train of three spiral washers containing concentrated sulphuric acid. The condenser, C, was then charged to 8300 volts, and the potential maintained constant at this value by balancing out leakage losses by varying the impedance of the diode. On suitably decreasing the gap in the explosion vessel, a spark passed. According as whether ignition took place or not, the experiment was repeated with the explosion vessel filled to either a lower or higher pressure than previously. In this manner a " bracket " was found such that at the lower pressure ignition failed to occur when five sparks were passed at 30-second intervals, but was brought about at the higher pressure by one, usually the first, of three such spaced sparks. With the mica dielectric condensers the width of such a bracket could be reduced to less than 0·5 cm. provided the ignition pressures were above about 68 cm., below which it tended to widen with decreasing pressure to as much as between 2 and 3 cm. at 50 cm. Similarly, in the case of experiments carried out with the paper dielectric condensers, the bracket width amounted in some cases to as much as 3·5 cm. In what follows the mean value of a bracket is referred to as the "least igniting pressure."

Having in this manner obtained a measure of the igniting power of a spark, the gap in the vessel, B, was adjusted until the condenser, previously charged to 8300 volts, discharged across it; whereupon the impedance of the diode was reduced to such an extent as to permit of the passage of a train of 50 sparks at ½-second intervals. The resulting deflection, read off the micro-ammeter, A, was corrected by means of a cooling curve and thus afforded a rough, but for the present purposes sufficiently accurate, relative measure of the amount of energy dissipated by one spark.

The electrode surfaces were refaced after each experiment in order to remove possible pit marks.

Experimental Results.

Series I.—The results obtained with the mica dielectric condensers are recorded in Table I.

Table I.

$C/\mu F$.	$\frac{1}{2}CV^2$ Joules.	L coil turns.	Frequency k.c./s.	$i_{\max}$. amperes (calc.)	Least igniting pressure, cm.	Energy dissipated by discharge.
0·041	1·43	2	720	1540	>76·0	Decreased with decreasing frequency.
		4	590	1260	>76·0	
		6	500	1070	75·8	
		8	440	940	74·9	
		10	400	856	74·0	
		12	360	770	71·5	
		14	340	728	70·0	
0·051	1·76	2	650	1735	>76·0	Decreased with decreasing frequency.
		4	550	1465	76·0	
		6	450	1200	64·6	
		8	400	1068	73·8	
		10	360	950	70·5	
		12	320	855	65·0	
		14	300	800	64·4	
0·066	2·30	2	570	1965	75·6	Decreased with decreasing frequency.
		4	470	1620	75·7	
		6	400	1380	73·8	
		8	350	1210	69·3	
		10	320	1105	66·8	
		12	290	1000	59·4	
		14	270	930	56·5	
0·071	2·45	6	380	1430	73·1	Decreased with decreasing frequency.
		8	340	1265	66·6	
		14	260	970	50·0	

Series II.—The results tabulated in Table II were obtained with the two 0·2 μF Mansbridge type condensers, the capacities available being 0·1, 0·2 and 0·4 μF.

Table II.

$C/\mu F$.	$\frac{1}{2}CV^2$ Joules.	L coil turns.	Least igniting pressure, cm.	Energy dissipated by the discharge.
0·1	3·5	6	75·0	Decreased with increase in L.
		14	55·0	
0·2	7·0	6	65·5	Decreased with increase in L.
		14	47·0	
0·4	14·0	6	62·0	Decreased with increase in L.
		14	43·0	

Discussion.

It will be seen that, in each group of experiments, where the energy stored in the condenser was constant, the igniting power of the discharge increased with decreasing frequency, in spite of the fact that the energy actually dissipated by the spark decreased. Further, on comparing the results of, for example, the first and last groups of experiments in Table I, it is evident that the igniting power of the spark was chiefly determined by the natural frequency of the discharge circuit and only to a minor extent by the amount of energy originally stored in the condenser.

Therefore, the results set forth above prove that, under the conditions in question, (i) the igniting power of a spark due to the discharge of a condenser through an inductive circuit increases with increasing value of the inductance; (ii) the amount of energy dissipated by the spark decreases as the natural frequency of the circuit is decreased by increasing its inductance; and (iii) the discharge circuit frequency exerts a far greater influence on the igniting power of the spark than does the potential energy stored in the condenser prior to discharge. It follows, therefore, that the igniting power of a condenser discharge can and does increase with decrease in either the rate or amount of total energy dissipation in the discharge, provided the frequency of the discharge circuit be suitably reduced.

In order to examine the effect of the changes of frequency in our experiments upon the first part of the discharge it suffices to consider, for example, the conditions pertaining to the experiments of Series I.

The steady current resistance of the oscillation circuit, comprising mica dielectric condensers and a 14-turn coil, but excluding the spark gap, was approximately equivalent to that of 380 cm. of copper tubing of the dimensions previously given. The corresponding high-frequency resistance, when $C=0\cdot041$ μF, would be about 11 times greater. Of the condenser discharge spark it is well known that, since the voltage-current characteristic is negative, the resistance varies in some manner inversely with the current, and, further, that the R.M.S. voltage across the gap during discharge is either of the same order as that of the cold cathode potential fall, *i.e.*, about 300 volts, or less. Thus, under the conditions of the experiments of Series I, the total circuit resistance immediately after the beginning of a discharge must have been of the order of, or less than, 1 ohm. The resistance necessary for critical damping of a circuit, where $n = 340$ k.c./s. and $C = 0\cdot041$ μF, is 23 ohms. Hence, with sufficient accuracy, in each group of the experiments under consideration,

$i_{\text{max.}}$, the peak current of the first half oscillation, is directly proportional to the frequency, because CV is constant. Further, on comparing experiments such as, for instance, the third in the first, and the fourth in the second group in which the frequency was changed in such a manner that the ratio, L_1 (the total circuit inductance)/C, and hence also $i_{\text{max.}}$, was constant, it will be seen that the igniting power still increased with decreasing frequency. Therefore, the igniting power of the spark is not determined by the value of the peak current.

It has been shown experimentally above that, under conditions where CV was constant, the total energy dissipated by the discharge decreased throughout with decreasing frequency. It follows that, in each individual group of the experiments under consideration, the decremental spark losses and also the corresponding rate of dissipation of energy by the discharge decreased with decreasing frequency. But in each such group the igniting power of the discharge increased with decreasing frequency.

To sum up. It has now been shown that, under the conditions in question, the igniting power of a spark due to the discharge of a condenser through an inductive circuit is determined by the natural frequency of the circuit to such an extent that a suitable decrease in frequency may completely outweigh the effect of any possible reduction in igniting power due to either a decreased amount or rate of energy dissipation, or both, by either the first half oscillation of a spark or by the entire discharge. According to the thermal theory, however, " ignition depends on the heating of a sufficient volume of the gas by conduction to a sufficient temperature,"* which also implies that " the heat energy required in the source to produce ignition is least when the heat is imparted instantaneously. When the rate of heat supply is less, a greater quantity of heat must be given to the gas before ignition can occur."† Hence it is clear that the conflict between the thermal theory and the facts set forth herein is complete. Therefore, the mechanism of electric spark ignition, and indeed of ignition as a whole, cannot be adequately explained in terms of any purely thermal theory.

On the other hand, the electrical hypothesis is consistent with, and capable of explaining, all known facts relating to the ignition of gases. For, according to this view, ignition being primarily determined by the setting up of a sufficient concentration of suitably activated constituent molecules, the imparting of energy to the molecules in such a manner as to bring about either an insufficient or excessive degree of activation is wasteful from the point of view of causing ignition. Now, it is well known that the greater the frequency of a condensed discharge the higher is the level to which the molecules are thereby activated. Thus the high-frequency spark is in general a rich source of ionisation, whereas the low-frequency arc spectrum reveals mainly the presence of neutral atoms or molecules. Further, we have shown previously* that the cathodic combustion of carbonic oxide " detonating gas " is determined by a prior activation which falls short of complete ionisation of the carbonic oxide.

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* Morgan, 'Phil. Mag.,' vol. 11, p. 158 (1931).

† Morgan, 'Phil. Mag.,' vol. 45, p. 968 (1923); see also Taylor-Jones, Morgan and Wheeler, *loc. cit.*

In view of the foregoing facts and considerations, we conclude that ignition is determined by the setting up of a sufficient concentration of suitably activated molecules, and that in our experiments a reduction in frequency resulted in an increase in the ratio between energy usefully expended in the production of suitably activated molecules and that otherwise dissipated.

Our thanks are due to the Government Grants Committee of the Society, and to Messrs. Ferranti, Ltd., for grants which have defrayed part of the cost of this investigation.

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* 'Proc. Roy. Soc.,' A, vol. 129, p. 314 (1930).

Elastic Collisions.

By J. S. Townsend, F.R.S., Wykeham Professor of Physics, Oxford.

(Received July 17, 1931.)

1. In a recent paper by Bullard and Massey* on the "Elastic Scattering of Slow Electrons in Argon," the description they give of previous work on this subject is in many respects inaccurate and misleading. Similar faults also appear in some other papers published in the 'Proceedings,' where effects obtained in collisions of slow electrons with atoms or molecules of gases are described. It is therefore desirable to make clear the objections that have been raised to these papers, by considering a few cases in detail, and to refer briefly to some of the principal experiments by which the properties of slow electrons were discovered.

2. The collisions of electrons with molecules of gases in which the electrons lose only a small part of their energy, are generally known as elastic collisions. They were first observed in the experiments on the motion of electrons in air and other gases at low pressures, which were made at Oxford. The experiments were interpreted by the ordinary principles adopted in the kinetic theory of gases. The mean energy of agitation, E, of the electrons was thus obtained from the partial pressure of the electrons.† The theory of the motion was fully investigated by Pidduck.‡ He gave a method of finding the coefficient of elasticity in the collisions of electrons with molecules or atoms of a gas, and he showed that in air the collisions were almost the same as the collisions of perfectly elastic spheres.

The mean loss of energy, λE, of an electron in a collision, and the mean free path, l, of an electron are easily obtained from these experiments.

3. In a paper by Atkinson on "Statistical Experiments on the Motion of Electrons in Gases,"§ it is stated that our method of finding the average loss of energy of electrons is erroneous; one of the reasons given is that in many cases with helium we obtained the value $2\cdot5 \times 10^{-4}$ for λ, which is 10 per cent. less than the "correct" value, $2\cdot73 \times 10^{-4}$. These investigations are then

* Bullard and Massey, 'Proc. Roy. Soc.,' A, vol. 130, p. 579 (1931).

† J. S. Townsend, 'Proc. Roy. Soc.,' A, vol. 81, p. 464 (1908).

‡ F. B. Pidduck, 'Proc. Roy. Soc.,' A, vol. 88, p. 296 (1913).

§ 'Proc. Roy. Soc.,' A, vol. 119, p. 335 (1928).

dismissed with the following remark: "The exact cause of the error need not be enquired into here, but the fact that such a serious error has been overlooked cannot but create a suspicion that in more obscure cases also, such as the calculations of mean free paths, agitation energies and so on, equally essential considerations may have been omitted."

There is a marked difference between this reference to our work and the references to work which has been done elsewhere. This may be seen by considering the account given in Atkinson's paper of the work of Hertz and of Benade and Compton on the loss of energy of electrons in collisions with atoms of helium.

It is there stated that they obtained values of λ for helium which are in good agreement with the theoretical value. In a footnote the correct theoretical value of λ is said to be $2 \cdot 73 \times 10^{-4}$, and the number calculated by Hertz from the experiments is given as $2 \cdot 7 \times 10^{-4}$. There is no mention of any uncertainty about this result, or of the statements of Franck and Jordan made in their book,* "Anregung von Quantensprungen durch Stosse," as to the accuracy to be expected in estimating λ by the methods due to Hertz.

4. The following are the conclusions arrived at by Franck and Jordan with regard to the works of Hertz and of Benade and Compton on this subject. On p. 42 of their book it is stated that the values of λ derived from one set of investigations fluctuate between the values $1 \cdot 2 \times 10^{-4}$ to 3×10^{-4}. On p. 49 it is stated that values of λ derived from another set of investigations lie between the limits 3×10^{-4} and 8×10^{-4}. They state that the latter results agree with the theory of elastic collisions to the degree of accuracy which is to be expected. This degree of accuracy is indicated on p. 48, where it is stated, "We can therefore at best expect an agreement only in order of magnitude between the values of λ calculated from experimental data and the theoretical value $2 \cdot 9 \times 10^{-4}$."

Franck and Jordan do not refer to the experiments made at Oxford, which have been interpreted by the ordinary kinetic theory. These experiments give more consistent and reliable results than those described in their book. This may be seen from the figures given in Table I in the paper on the motion of electrons in helium,† or from the table of values of λ given by Bailey‡ which were obtained by our method.

5. In the paper by Bullard and Massey on "The Elastic Scattering of Slow

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* Julius Springer, Berlin, 1926.

† J. S. Townsend and V. A. Bailey, 'Phil. Mag.,' vol. 46, p. 657 (1923).

‡ V. A. Bailey, 'Phil. Mag.,' vol. 11, p. 1052 (1931).

Electrons in Argon," there is no mention of the work done at Oxford. They refer to the variation of the effective cross section of atoms with the velocity of the electrons as the " Ramsauer effect," and on p. 579 it is stated, " However the investigations of Ramsauer and others on the total absorbing cross sections of atoms for slow electrons (2 to 30 volts) have shown that at these velocities a very peculiar variation of cross section with velocity occurs. In particular, for the rare gases a pronounced maximum and minimum are observed."

There are several mistakes in this statement, as may be seen by referring to the paper published in the 'Annalen der Physik' by Brose and Saayman.* This paper contains an account of the principal determinations of the effective cross section by the different methods and gives the references to the original papers.†

The results of our determinations of the free paths are given by Brose and Saayman in terms of the effective cross section, so that they may be compared with the cross sections obtained by other methods.

In neon and helium no maximum values of the mean free paths have been observed, but there are maximum and minimum values in many ordinary gases as well as in argon.

6. For example, in hydrogen, nitrogen and oxygen,‡ minima values of the mean free paths have been observed for electrons with small energies from 1·5 to 3 volts. In carbon dioxide§ the mean free path has a maximum value for electrons with the energy of 1·7 volts. Thus the general phenomena of maxima and minima cross sections were found at Oxford to be characteristic of various gases long before they were recognised as such elsewhere.

The experiments which we made to determine the mean free paths in argon for electrons with small energies, show that there is a maximum value of the free path for the energy 0·39 volt. The large values of the mean free paths which were obtained with energies of that order are shown by the following table,‖ where the energies, E, of the electron are given in volts, the mean free paths l_A of the electrons in argon at 1 mm. pressure, and the mean free paths l_H in hydrogen are given in centimetres.

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* Brose and Saayman, 'Ann. Physik,' vol. 5, pp. 797–852 (1930).

† Ramsauer admits that the historical development of the whole field as given by Brose and Saayman has on the whole been correctly represented; see 'Ann. Physik,' vol. 6, p. 903 (1930).

‡ J. S. Townsend and V. A. Bailey, 'Phil. Mag.,' vol. 42, p. 873 (1921).

§ M. F. Skinker, 'Phil. Mag.,' vol. 44, p. 994 (1922).

‖ J. S. Townsend and V. A. Bailey, 'Phil. Mag.,' vol. 46, p. 1034 (1922).

E	0·15	0·22	0·30	0·37	0·48	0·59	0·74
$l_A \times 10^2$	113	138	154	161	154	138	110
$l_H \times 10^2$	3·62	3·3	3·0	2·9	2·7	2·5	2·3

E	1·11	1·48	1·85	2·6	3·7	5·2
$l_A \times 10^2$	61·5	39·5	29·5	20	13·6	10·4
$l_H \times 10^2$	2·0	2·0	2·0	2·3	3·0	4·0

The maximum value of the mean free path in argon indicates a marked minimum in the angular deflections of electrons in the collisions with atoms of the gas.

The mean free paths of electrons obtained by these experiments may be compared with the values obtained from the theory of viscosity. Assuming the molecules to resemble smooth elastic spheres, of radius σ, the mean free path l of an electron would be $1/\pi\sigma^2N$, and the mean free path l' of a molecule of a gas would be $1/\sqrt{2}\,4\pi\sigma^2N$. Thus the mean free path of an electron obtained from the theory of viscosity is $5{\cdot}6 \times l'$.

The value of this quantity ($5{\cdot}6 \times l'$) for air at 1 mm. pressure is 0·039 cm. The mean free path of electrons in air has a minimum value 0·027 cm. for electrons with the energy 2 volts. As the energy diminishes, l increases and the mean free path for electrons with energies of about 0·2 volt is 0·034, which is approximately the same as the mean free path obtained from the theory of viscosity.* This result is of interest although the formulæ for the mean free paths are only approximations.

In hydrogen the minimum value of l, 0·02 cm., is one quarter of the value found from the viscosity, and in argon the maximum value of l, 1·61 cm., is forty times the value found from the viscosity.

7. In his early experiments, which were made about the same time as ours, Ramsauer observed small changes in the effective cross section in helium and neon and large changes in argon, as the energy of the electrons is reduced. A pronounced maximum value† of the cross section was obtained in argon for electrons with energies of about 14 volts, but in these experiments no minimum value of the cross section was observed. The cross section for electrons with energies of 0·75 volt was found to be about one-seventh of the value deduced

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* J. S. Townsend and H. T. Tizard, 'Proc. Roy. Soc.,' A, vol. 88, p. 336 (1913).

† C. Ramsauer, 'Ann. Physik,' vol. 66, p. 546 (1921).

from the theory of viscosity. Ramsauer and others concluded from this, that the effective cross section of argon tended to vanish as the energy of the electrons became very small. In some of the papers on Ramsauer's work, the vanishing values of the cross section were calculated, by extrapolation, for very small values of the energy.

Subsequently, in 1929, further experiments were made by Ramsauer and Kollath,* with electrons with energies less than 0·75 volt. They then found that the cross section did not diminish as the energy became very small, but it attained a minimum value for electrons with the energy 0·37 volt. This was treated as a new discovery until it was pointed out by Brose and Saayman that the result is in accordance with our experiments published in 1922, where we found a maximum value of the mean free path in argon for electrons with the energy 0·39 volt.

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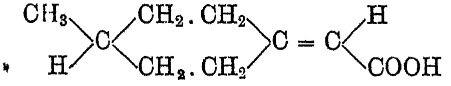
* C. Ramsauer and R. Kollath, 'Ann. Physik,' vol. 3, p. 536 (1929).

The Optically Active spiro-5 : 5-*Dihydantoins.*

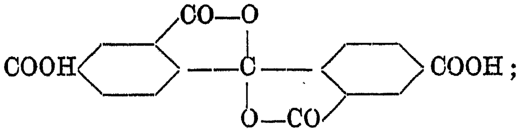
By Sir WILLIAM JACKSON POPE, K.B.E., F.R.S., and JAMES BELL WHITWORTH, Ph.D.

(Received August 3, 1931.)

The first substance to be obtained, showing optical activity in the amorphous state but containing no asymmetric atom in the molecule, was the 1-methyl*cyclo*hexylideneacetic acid,



of Perkin and Pope,* the resolution of the synthetic material being effected by Perkin, Pope and Wallach.† In a later paper‡ Perkin and Pope showed that the optical activity persists in a remarkable way throughout a series of reactions. At that time it was recognised that certain types of carbospiranes should be similarly resolvable into optically active components, but the first case of this kind to be realised was that of the keto-dilactone of benzophenone-2 : 4 : 2′ : 4′-tetracarboxylic acid prepared by Mills§



the resolution was effected by Mills and Nodder.||

The work of Mills and Nodder established the stereochemical principle involved, but the compounds used in this and similar later investigations¶ are of complex constitution and do not lend themselves readily to the study of the effects of substitution or tautomeric change on the optical activity. We consequently prepared the *spiro*-5 : 5-dihydantoin described by H. Biltz, Heyn and Bergius,** and succeeded in resolving the synthetic compound into its optically active components by crystallisation with brucine.

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* 'Trans. Chem. Soc.,' vol. 93, p. 1075 (1908).

† 'Trans. Chem. Soc.,' vol. 95, p. 1789 (1909).

‡ 'Trans. Chem. Soc.,' vol. 99, p. 1510 (1911).

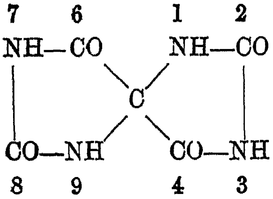
§ 'Proc. Camb. Phil. Soc.,' vol. 18, p. 149 (1915).

|| 'Trans. Chem. Soc.,' vol. 117, p. 1407 (1920), and vol. 119, p. 2094 (1921).

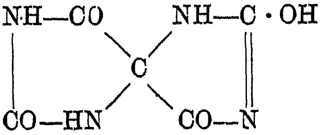
¶ Leuchs, Conrad and Katinsky, 'Ber. Deuts. Chem. Ges.,' vol. 55, p. 2131 (1922).

** Liebig's 'Annalen,' vol. 413, p. 79 (1916).

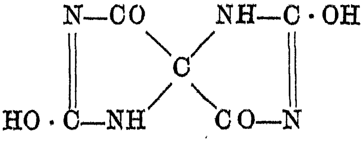
In accordance with modern views this substance should exist in the ketonic form (1), but in its salts would be expected to assume one or both of the enolic forms (2 and 3); obvious alternatives to these tautomeric formulæ might be suggested.



(1)



(2)



(3).

The molecular configuration of this very simple spirane in the forms (1) and (3), like that of the keto-dilactone of Mills and Nodder, should possess an axis of two-fold symmetry but neither a centre or planes of symmetry; the two wings of the molecule may be supposed to lie at right angles to each other. Whilst neither of these forms contains an asymmetric carbon atom, such an asymmetric atom is present in form (2); this configuration therefore possesses no elements of symmetry.

Three tautomeric forms of the *spiro*-5 : 5-dihydantoin may thus exist and each should occur in two enantiomorphously related isomerides; it is interesting to note that the determinations of the rotatory dispersion of the dihydantoin, measured under different conditions and recorded later in this paper, indicate that the substance exists in three forms. It is perhaps premature to attempt at this stage to allocate each of the three theoretically possible constitutions to one of the three modifications which have been thus experimentally distinguished; certain conclusions can, however, be definitely drawn. It will be seen from the tables given later that the specific rotations and the rotatory dispersions of dextro-*spiro*-5 : 5-dihydantoin are almost the same in ethyl alcohol, water and pyridine solutions, the values for λ_0 being 2453, 2436 and 2457 Å.U. respectively; it may be concluded that the substance exists in one specific form, presumably the ketonic form (1), in these three solvents. When the dihydantoin (1 mol.) is dissolved in aqueous soda (1 mol.) the rotatory power falls to roughly one-half; since the rotatory dispersion remains normal, with $\lambda_0 = 2037$ Å.U., it would seem likely that the substance is present in another form, possibly the keto-enolic form (2); in any case it is improbable that the dihydantoin is present as a mixture of the two forms (1) and (3). When the *d*-*spiro*-5 : 5-dihydantoin (1 mol.) is dissolved in sufficient aqueous soda

(2 mols.) to form the di-enolic form (3) it becomes lævo-rotatory; the rotatory dispersion becomes quite abnormal and no single value for λ_0 can be calculated. In this concentration of soda the rotatory powers did not change whilst the measurements were being made. Since it is conceivable that the addition of two molecular proportions of soda is insufficient to convert the whole of the dihydantoin into the di-enolic form (3), measurements of the rotatory powers were made in aqueous solutions containing twice that proportion of soda, namely, 4 molecules; the rotatory powers, determined in the freshly made solution, were practically identical with those obtained in the solution containing two molecular proportions of soda. It may be noted, however, that the rotatory powers diminish very slowly when the stronger soda solution is kept; this is due to hydrolysis and opening of the rings in the molecule.

The resolution of the *dl-spiro*-5 : 5-dihydantoin proceeds in what appears to be a unique manner. In order to get this sparingly soluble substance into solution it is necessary to boil it (1 mol.) with an alcoholic solution of brucine (2 mols.); on cooling, a salt consisting of 1 molecule of brucine with one of lævo-*spiro*-5 : 5-dihydantoin separates in an almost pure state. On allowing the filtrate from this salt to stand, a salt consisting of 2 molecules of brucine with 1 of dextro-*spiro*-dihydantoin is deposited and again in a practically pure state. It is thus possible to obtain the *d*- and *l*-isomerides in an optically pure condition with the use of the same alkaloid. It seems that of the four salts of the acid (A) and the base (B) which can be formed, namely, 1B — A, 1B + A, 2B — A and 2B + A, the first separates almost quantitatively during the initial boiling up and cooling, so that the third never comes into question. The fourth, being less soluble than the second, then separates alone on allowing the mother liquor to stand.

The externally compensated *spiro*-5 : 5-dihydantoin crystallises without water of crystallisation, and is almost insoluble in the usual solvents excepting water; the optically active components are comparatively freely soluble and crystallise with 1 molecule of water.

It was at first suspected that one of the two rings had opened owing to partial hydrolysis by boiling with the brucine solution. This, however, is not the case because on mixing alcoholic solutions of the *d*- and *l*-isomerides the original racemic substance crystallises out immediately.

The anhydrous crystals of racemic *spiro*-dihydantoin have a density of 1·94; the hydrated crystals of the active components have a density of 1·76. These abnormally high densities are accompanied in the former case by very sparing solubility in water and by high melting point. Uric acid crystals have a density of 1·855–1·893,* are very sparingly soluble in water and do not melt on heating. These high densities indicate such a denseness of packing of the molecules in the crystal structure that the forces holding the crystal together are not easily overcome by solvents or by heat. It would be interesting to learn whether other sparingly soluble compounds of low molecular weight such as tetraketo-piperazine and urazole, which contain the group—CO . NH . CO—and show high melting points, also possess high densities in the crystalline state; the connection between density, solubility and melting point in compounds of this type seems hitherto to have escaped notice. It is noteworthy that cyanuric acid has a density of 2·500 at 19° and cyamelide a density of 1·974 at 0°.†

Experimental.

The *dl-spiro*-5 : 5-dihydantoin was prepared by condensing urea with alloxan as described by Biltz, Heyn and Bergius.‡ On crystallisation from boiling water it was obtained in thin, colourless plates which were anhydrous. (Found: C = 32·4; H = 2·2 per cent. $C_5H_4O_4N_4$ requires C = 32·6; H = 2·2 per cent.).

Several attempts were made to obtain good crystals, but in all cases they were small, ill-formed and unsuited to goniometric measurement. Dr. W. A. Wooster examined the crystals and reported that "under the microscope a good biaxial optic picture could be obtained. The acute bisectrix is inclined at about 30° to the length of the prism and the optic axial angle is about 40°. The double refraction is strong and positive in sign; no pyroelectric properties were noted."

Mr. J. D. Bernal has determined the X-ray reflections of the crystals of racemic *spiro*-5 : 5-dihydantoin and has supplied the following particulars. "The lattice is the *c*-face centred monoclinic.

$$a = 6\cdot0;\ b = 11\cdot3;\ c = 9\cdot25 \text{ Å.U.}\quad \beta = 105^\circ\ 30'.$$

The crystal cell consists of 4 molecules; the calculated density is 2·00 and the observed density is 1·94. The space group is C_{2h}^6–$C2/c$ and the molecule has a diad axis of symmetry. The molecules are arranged in two layers parallel to the pinacoid-*c*; these correspond to the four layers of the optically active form and are of the same thickness, namely, d_{002} = 4·46 Å.U. for the racemic substance and d_{004} = 4·48 Å.U. for the *l*-component. In the racemic substance alternate layers consist of *d*- and *l*-molecules ; the molecules in each layer are considerably more closely packed than in the optically active form. The two rings composing the molecule lie approximately at right angles to one another and interleave with the rings in neighbouring layers in a similar way to that of the active form (fig. 1). The acute bisectrix (slowest vibration direction) lies nearly exactly along the *c*-axis and thus, as in the active form, is parallel to the planes of the rings. The presence of molecules of the *d*- and *l*-configuration, alternately placed, permits of closer packing in the racemic than in the active forms and thus gives rise to the lower solubility of the former compound. The exceptionally high density of the racemic substance

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* Schröder, 'Ber. Deuts. Chem. Ges.,' vol. 13, p. 1072 (1880).

† Troost and Hautefeuille, 'C. R. Acad. Sci. Paris,' vol. 69, p. 50 (1869).

‡ Liebig's 'Annalen,' vol. 413, p. 80 (1916).

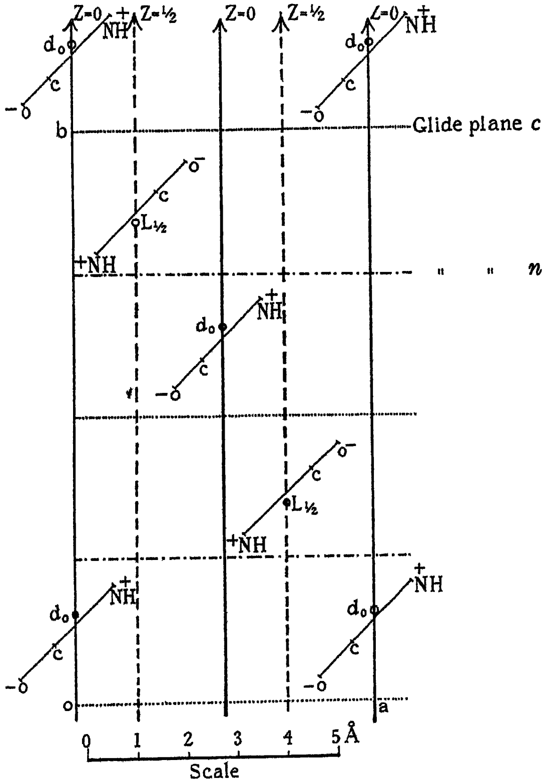
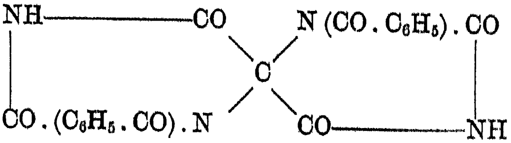


FIG. 1.—Section of racemic spirodihydantoin parallel to *c* pinacoid at height ¼ above base of cell. The tops of the upper rings of the molecules in the lower layer are shown lying between the bottom edges of the lower rings of the molecules in the intermediate layer. Diad axes in the base of the cell and at height ½ are shown by ⋙Θ➝ and ⋙—Θ-➝ respectively. The centres of the *d*- and *l*-molecules, lying in the base of the cell and at height ½, are marked d_0 and $l_{½}$ respectively.

is undoubtedly due to the strongly polar nature of the NH and CO groups and to the absence of methylenic hydrogen atoms; similar properties are observed with 2 : 5-diketopiperazine* and uric acid."

The diacetyl derivative was obtained by boiling with a very large excess of acetic anhydride,† but is more easily prepared by boiling the parent substance (0·3 gram) with a 12 per cent. solution (8 c.c.) of acetic anhydride in dry pyridine for half-an-hour. After evaporating *in vacuo* on the water-bath the crystalline residue is recrystallised from hot water and obtained in small colourless prisms containing water of crystallisation and melting at 248–249°. (Found: $C = 37 \cdot 7$; $H = 3 \cdot 6$ per cent. $C_9H_8O_6N_4$, H_2O requires $C = 37 \cdot 8$; $H = 3 \cdot 5$ per cent.). Biltz at first thought this to be the 2 : 8-diacetic ester derived from the dienolic form (3) but has recently decided‡ that it is the 1 : 9-diacetyl derivative of the form (1); it is freely soluble in dilute soda, ammonia or sodium carbonate and is precipitated unchanged on acidification.

dl-1 : 9-*Dibenzoyl*-spiro-5 : 5-*Dihydantoin.*



Benzoyl chloride (1 c.c.) is slowly added, with shaking, to an ice-cold solution of the *spiro*-dihydantoin (0·3 gram) in dry pyridine (10 c.c.); a crystalline material, probably pyridine hydrochloride, separates. After standing, the solution is filtered and the solvent distilled off *in vacuo*; the residual gum crystallises on standing and on recrystallisation from dilute aqueous acetone the dibenzoyl-derivative (0·3 gram) is obtained in short, colourless needles which on rapid heating darken at 290° and melt at 295° with decomposition. It is readily soluble in acetone, alcohol, ether, ethyl acetate and pyridine but very sparingly in water, benzene and chloroform. The compound is freely soluble in dilute cold soda, ammonia or sodium carbonate and separates unchanged on acidification; it therefore doubtless has the constitution assigned to it above. (Found: $C = 58 \cdot 3$; $H = 3 \cdot 2$ per cent. $C_{19}H_{12}O_6N_4$ requires $C = 58 \cdot 3$; $H = 3 \cdot 1$ per cent.).

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* J. D. Bernal, 'Z. Kryst.,' vol. 78, p. 363 (1931).

† Biltz and Klemm, Liebig's 'Annalen,' vol. 448, p. 134 (1926).

‡ 'Ber. Deuts. Chem. Ges.,' vol. 64, p. 1149 (1931).

Resolution of dl-spiro-5 : 5-*Dihydantoin.*

The racemic spirane (7·4 gram) is added gradually to a warm solution of brucine (37 gram) in rectified spirit (650 c.c.); mono-brucine *l-spiro*-5 : 5-dihydantoin soon begins to separate. After gently boiling for 3 hours and allowing to cool, the salt (12 gram; theoretical 12·3 gram) is collected and recrystallised once from boiling water (750 c.c.). The optically pure salt (8 gram) is thus obtained in clusters of soft, colourless needles which melt at 259–260° with decomposition; it contains 2 molecules of water of crystallisation which are lost at 125–135° *in vacuo*. (Found, after standing in a vacuum desiccator over sulphuric acid: $C = 54{\cdot}9$; $H = 5{\cdot}6$; $H_2O = 5{\cdot}5$ per cent. $C_{28}H_{30}O_8N_6 . 2H_2O$ requires $C = 54{\cdot}8$; $H = 5{\cdot}6$; $H_2O = 5{\cdot}9$ per cent.). The salt is sparingly soluble in alcohol and acetone and practically insoluble in chloroform and benzene.

The alcoholic mother liquor from which the above salt has separated deposits the di-brucine salt of *d-spiro*-5 : 5-dihydantoin in small, lustrous, colourless plates (15 gram; theoretical 20 gram); the salt is generally optically pure, or is obtained optically pure by one recrystallisation from alcohol, and melts at 205–206° with decomposition. A further quantity (4 gram) of impure salt is obtained on concentration of the mother liquor. It is fairly soluble in water and alcohol, sparingly in acetone and almost insoluble in chloroform; the crystals appear to contain two molecular proportions of water of crystallisation, but only 1½ molecules were removed on heating *in vacuo* at 120–130°. (Found, after drying *in vacuo* over sulphuric acid: $C = 61{\cdot}0$; $H = 6{\cdot}2$; $H_2O = 2{\cdot}7$ per cent. $C_{51}H_{56}O_{12}N_8 . 2H_2O$ requires $C = 60{\cdot}8$; $H = 6{\cdot}0$; $2H_2O = 3{\cdot}6$ per cent.) It has $[\alpha]_{5780}^{18^\circ} = -38^\circ$, $[\alpha]_{5461}^{18^\circ} = -45^\circ$ in water ($c = 0{\cdot}4969$ g./100 c.c.; $l = 4$.).

l-spiro-5 : 5-*Dihydantoin.*

The corresponding brucine salt (8 gram) is decomposed with aqueous-alcoholic ammonia, the brucine extracted with chloroform, and the filtered aqueous solution (20–25 c.c.) acidified with hydrochloric acid. The *l*-dihydantoin then slowly separates in short, colourless prisms; these are filtered off and washed with dilute hydrochloric acid, water, and alcohol-ether and dried in a vacuum desiccator. The compound so obtained (2 gram) darkens at 240° and does not melt at 320°; it contains water of crystallisation ($1H_2O$), which is readily removed on heating at 120°, or at 100–110° in a vacuum. (Found: $C = 29{\cdot}7$; $H = 3{\cdot}1$; $H_2O = 8{\cdot}9$ per cent. $C_5H_4O_4N_4 . H_2O$ requires $C = 29{\cdot}7$; $H = 3{\cdot}0$; $H_2O = 8{\cdot}9$ per cent.; found in the anhydrous material:

C = 32·6; H = 2·3 per cent. $C_5H_4O_4N_4$ requires C = 32·6; H = 2·2 per cent.).

l-spiro-5 : 5-dihydantoin is very readily soluble in alcohol, acetone or pyridine, less readily soluble in water and practically insoluble in ether, benzene or chloroform. The hydrated material gave $[\alpha]^{17°}_{5780} = -98°$, $[\alpha]^{17°}_{5461} = -113°$ in ethyl alcohol ($l = 2$; $c = 1·449$ g./100 c.c.), $[\alpha]^{19°}_{5780} = -98°$, $[\alpha]^{19°}_{5461} = -113°$ in water ($l = 4$; $c = 0·5257$ g./100 c.c.), $[\alpha]^{17°}_{5461} = +9°$ in 12 per cent. aqueous ammonium hydroxide ($l = 2$; $c = 1·7265$ g./100 c.c.), $[\alpha]^{18°}_{5461} = +7°$ in 10 per cent. aqueous potassium hydroxide ($l = 2$; $c = 1·1615$ g./100 c.c.). The rotatory power of the ethyl alcohol and water solutions remained unchanged after standing for several days, while the solution in potassium hydroxide became inactive on boiling.

Dr. W. A. Wooster has examined the crystals of *l*- and *d-spiro*-5 : 5-dihydantoin and reports that "they occur in well developed tetragonal bipyramids modified at the ends by basal planes and are the same whether grown from water, alcohol or acetone. The forms observed are {001} and {101} and the habit of the crystals is indicated in the figure (fig. 2). The dextro- and lævo-forms were quite alike in general appearance and in the angle (001) : (101) = 70° 21′. The axial ratio $c : a = 2·800$.

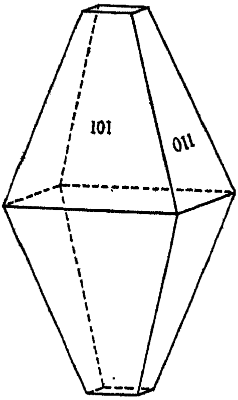


FIG. 2.

"The faces (101), ($\bar{1}01$) formed an excellent natural prism by means of which the indices of refraction were determined as $\omega_{Na} = 1·555$, $\varepsilon_{Na} = 1·720$. The crystals are therefore optically positive and of high double refraction. By examining some fragments immersed in a liquid of about the same refractive index a uniaxial optic picture was observed; the black brushes passed through the centre of the rings and showed no sign of rotatory polarisation in the crystals. No cleavage or pyroelectricity was observed."

Mr. J. D. Bernal has determined the X-ray reflections of the hydrated crystals of *l-spiro*-5 : 5-dihydantoin and furnishes the following particulars. "The crystal lattice is the simple tetragonal and the crystal cell consists of four molecules; the molecular symmetry is characterised by a diad axis only.

"$a = 6·40$; $c = 17·95$ Å.U. Space group, $D_4{}^3 - P4_12$. The calculated density is 1·81 and the observed density 1·76.

"The molecules are arranged in four layers related to each other by the tetrad screw axis. The evidence from the intensities of X-ray reflection suggests that the two rings of each molecule lie at right angles to each other and parallel to the tetrad screw axis. In this way the upper rings of the molecules in one layer lie parallel to and between the lower rings in the layer next above; as all the molecules are of the lævo-configuration the negative charge on any oxygen atom is thus enabled to be neutralised by the positive charges of the NH groups which surround it in square array as in the pinacoid planes of rock salt (fig. 3). The water molecules serve to fill in the gaps in the structure

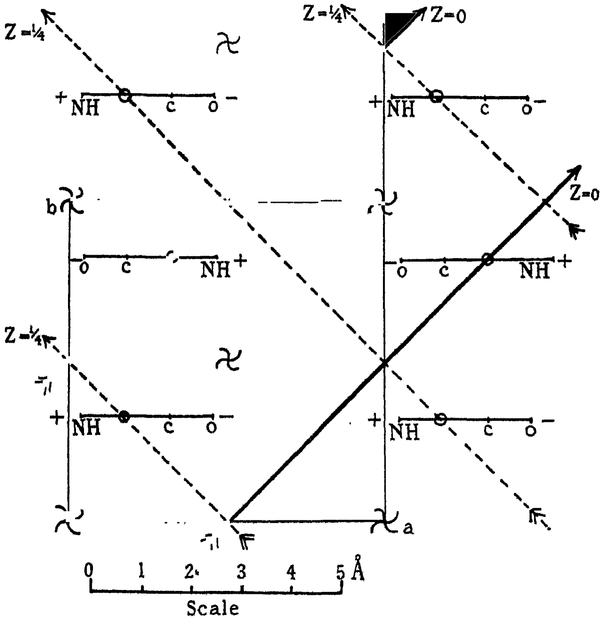


Fig. 3.—Section of 1-*spiro*-dihydantoin parallel to the *c* pinacoid at a height 1/8 above the base of the cell. The tops of the upper rings of the molecules in the lowest layer are shown lying between the bottom edges of the lower rings of the molecules in the next layer. Diad axes in the base of the cell are shown thus ⋙⊖→ and ¼ above it thus ⋙—⊖→. Tetragonal screw axes perpendicular to the base are shown thus ⊹.

which probably lie on the diad axes between neighbouring dihydantoin molecules. In this way an extremely compact pseudoionic structure is built up; this accounts for the high melting point and density of the crystals. As all the rings lie parallel to the *c*-axis the strong positive birefringence is well explained; it is noteworthy that the birefringence is of the same order of magnitude as that of calcite.

"It is of interest that the *spiro*-5 : 5-dihydantoin provide another example of substances of which the enantiomorphous molecules have an axis of symmetry and in which the optically active forms have high (tetragonal) symmetry while the more stable racemic form has only monoclinic symmetry. This case thus resembles that of the cystines (J. D. Bernal, *loc. cit.*) in respect of the symmetry relations (with the difference that *l*-cystine is hexagonal), and also in the remarkable fact that in both cases the optical activity of the *l*- (or *d*-) molecules is neutralised or compensated by their screw arrangement in the crystal structure. A complete account of these crystal structures will be published later."

On slow dehydration by heating, the transparent crystals become opaque without losing their form; the water of crystallisation is readily taken up again on exposure to moist air at room temperature, although the crystals remain opaque; 0·4772 gram of the anhydrous material absorbed 0·0466 gram H_2O (theoretical 0·0467 gram H_2O).

d-spiro-5 : 5-*Dihydantoin.*

This substance was separated from its dibrucine salt by the method used for obtaining the *l*-isomeride; it forms short, colourless prisms containing one molecule of water of crystallisation. (Found: $C = 29{\cdot}9$; $H = 3{\cdot}1$; $H_2O = 8{\cdot}9$ per cent.). The observed specific rotatory powers were almost identical, numerically, with those obtained for the *l*-isomeride. The hydrated substance gave in ethyl alcohol ($l = 2$; $c = 1{\cdot}3635$ g./100 c.c.) $[\alpha]_{5780}^{13{\cdot}5^\circ} = +98^\circ$, $[\alpha]_{5461}^{13{\cdot}5^\circ} = +112{\cdot}5^\circ$; in water ($l = 6$; $c = 0{\cdot}5808$ g./100 c.c.) $[\alpha]_{5780}^{20^\circ} = +99^\circ$, $[\alpha]_{5461}^{20^\circ} = +114^\circ$; in dilute aqueous sodium hydroxide (2 equivalents) ($l = 2$; $c = 2{\cdot}070$ g./100 c.c.) $[\alpha]_{5780}^{15^\circ} = -4{\cdot}1^\circ$, $[\alpha]_{5461}^{15^\circ} = -6{\cdot}3^\circ$, $[\alpha]_{4358}^{15^\circ} = -25^\circ$. The anhydrous substance gave in dry pyridine ($l = 6$; $c = 2{\cdot}079$ g./100 c.c.), $[\alpha]_{5780}^{20^\circ} = +107^\circ$, $[\alpha]_{5461}^{20^\circ} = +124^\circ$.

The following tables record the measurements of the rotatory dispersions of *d-spiro*-5 : 5-dihydantoin in a number of solvents; the conclusions which may be drawn from these results have been discussed earlier in this paper.

Rotatory Dispersion of *d-spiro*-5 : 5-Dihydantoin in Ethyl Alcohol at 20°.

2·0312 g. hydrated material per 100 c.c.; $l = 6$ dcm.; $[\alpha]_{5461}^{20^\circ} = + 112\cdot5^\circ$; $\alpha_{4358}/\alpha_{5461} = 1\cdot83$.

$\alpha = 3\cdot248/(\lambda^2 - 0\cdot0602)$. $\lambda_0 = 2453$ Å.U.

λ.	Å.U.	α obs.	α calc.	Diff.	λ.	Å.U.	α obs.	α calc.	Diff.
		°	°	°			°	°	°
Li	6708	+ 8·31	+ 8·34	−0·03	Ag	5209	+15·40	+15·39	+0·01
Cd	6438	+ 9·12	+ 9·17	−0·05	Cu	5153	+15·84	+15·82	+0·02
Zn	6362	+ 9·39	+ 9·42	−0·03	Cu	5105	+16·21	+16·21	±0
Li	6104	+10·39	+10·40	−0·01	Cd	5086	+16·38	+16·38	±0
Na	5893	+11·31	+11·32	−0·01	Zn	4810	+18·97	+18·98	−0·01
Cu	5782	+11·84	+11·85	−0·01	Cd	4800	+19·09	+19·09	±0
Hg	5780	+11·90	+11·85	+0·05	Zn	4722	+20·00	+19·95	+0·05
Cu	5700	+12·24	+12·27	−0·03	Zn	4680	+20·47	+20·45	+0·02
Hg	5461	+13·70	+13·65	+0·05	Cd	4678	+20·51	+20·48	+0·03
Cu	5219	+15·34	+15·32	+0·02	Li	4602	+21·41	+21·43	−0·02
					Hg	4358	+25·01	+25·04	−0·03

Rotatory Dispersion of *anhydrous d-spiro*-Dihydantoin in Dry Pyridine at 20°.

2·079 g. anhydrous material per 100 c.c.; $l = 6$ dcm.; $[\alpha]_{5461}^{20^\circ} = + 124^\circ$; $\alpha_{4358}/\alpha_{5461} = 1\cdot83$.

$\alpha = 3\cdot659/(\lambda^2 - 0\cdot0604)$ $\lambda_0 = 2457$ Å.U.

λ.	Å.U.	α obs.	α calc.	Diff.	λ.	Å.U.	α obs.	α calc.	Diff.
		°	°	°			°	°	°
Li	6708	+ 9·28	+ 9·39	−0·11	Hg	5461	+15·44	+15·39	+0·01
Cd	6438	+10·29	+10·33	−0·04	Cu	5219	+17·35	+17·26	+0·09
Zn	6362	+10·54	+10·62	−0·08	Cu	5153	+17·86	+17·83	+0·03
Li	6104	+11·61	+11·72	−0·11	Cu	5105	+18·26	+18·27	−0·01
Na	5893	+12·73	+12·76	−0·03	Zn	4810	+21·48	+21·40	+0·08
Cu	5782	+13·33	+13·36	−0·03	Cd	4800	+21·61	+21·53	+0·08
Hg	5780	+13·35	+13·37	−0·02	Zn	4722	+22·64	+22·51	+0·13
Cu	5700	+13·79	+13·83	−0·04	Zn	4680	+23·04	+23·07	−0·03
Ag	5468	+15·41	+15·35	+0·06	Hg	4358	+28·26	+28·26	±0

Rotatory Dispersion of *d-spiro*-5 : 5-Dihydantoin in Water at 20°.

0·5808 g. hydrated material per 100 c.c.; $l = 6$ dcm.; $[\alpha]^{20°}_{5461} = +114°$; $\alpha_{4358}/\alpha_{5461} = 1·80$.

$\alpha = 0·931/(\lambda^2 - 0·0593)$. $\lambda_0 = 2436$ Å.U.

λ.	Å.U.	α obs.	α calc.	Diff.	λ.	Å.U.	α obs.	α calc.	Diff.
		°	°	°			°	°	°
Li	6708	+2·35	+2·38	−0·03	Cu	5153	+4·54	+4·51	+0·03
Cd	6438	+2·62	+2·62	±0	Cu	5105	+4·63	+4·62	+0·01
Zn	6362	+2·70	+2·69	+0·01	Cd	5086	+4·67	+4·67	±0
Li	6104	+2·97	+2·97	±0	Zn	4810	+5·38	+5·41	−0·03
Na	5893	+3·24	+3·23	+0·01	Cd	4800	+5·46	+5·44	+0·02
Cu	5782	+3·41	+3·39	+0·02	Zn	4722	+5·65	+5·69	−0·04
Hg	5780	+3·46	+3·39	+0·07	Zn	4680	+5·74	+5·83	−0·09
Cu	5700	+3·51	+3·51	±0	Cd	4678	+5·77	+5·82	−0·05
Hg	5461	+3·98	+3·90	+0·08	Li	4602	+6·06	+6·11	−0·05
Cu	5219	+4·38	+4·37	+0·01	Hg	4358	+7·16	+7·13	+0·03
Ag	5209	+4·38	+4·39	−0·01					

Rotatory Dispersion of *d-spiro*-Dihydantoin in One Equivalent of Aqueous Sodium Hydroxide at 20°.

2·0742 g. hydrated material per 100 c.c.; $l = 6$ dcm.; $[\alpha]^{20°}_{5461} = +59·2°$; $\alpha_{4358}/\alpha_{5461} = 1·73$.

$\alpha = 1·889/(\lambda^2 - 0·0415)$. $\lambda_0 = 2037$ Å.U.

λ.	Å.U.	α obs.	α calc.	Diff.	λ.	Å.U.	α obs.	α calc.	Diff.
		°	°	°			°	°	°
Li	6708	+4·63	+4·63	±0	Cu	5219	+ 8·12	+ 8·18	−0·06
Cd	6438	+4·97	+5·07	−0·10	Cu	5153	+ 8·47	+ 8·43	+0·04
Zn	6362	+5·15	+5·20	−0·05	Cu	5105	+ 8·63	+ 8·62	+0·01
Li	6104	+5·71	+5·71	±0	Zn	4810	+ 9·97	+ 9·95	+0·02
Na	5893	+6·13	+6·18	−0·05	Zn	4722	+10·48	+10·41	+0·07
Cu	5782	+6·46	+6·45	+0·01	Cd	4678	+10·53	+10·65	−0·12
Hg	5780	+6·49	+6·46	+0·03	Li	4602	+11·17	+11·10	+0·07
Cu	5700	+6·68	+6·67	+0·01	Hg	4358	+12·74	+12·73	+0·01
Hg	5461	+7·36	+7·36	±0					

Rotatory Dispersion of *d-spiro*-Dihydantoin in Two Equivalents of Aqueous Sodium Hydroxide at 20°.

2·1066 g. hydrated material per 100 c.c.; l = 6 dcm.; $[\alpha]_{5461}^{20^\circ} = -6{\cdot}1^\circ$; $\alpha_{4358}/\alpha_{5461} = 4{\cdot}07$.

λ.	Å.U.	α obs.	α calc.	Diff.	λ.	Å.U.	α obs.	α calc.	Diff.
		°	°	°			°	°	°
Li	6708	−0·21	−0·37	+0·16	Ag	5209	−1·09	−0·95	−0·14
Li	6104	−0·39	−0·51	+0·12	Cd	5086	−1·22	−1·06	−0·16
Hg	5780	−0·55	−0·62	+0·07	Li	4602	−2·28	−1·93	−0·35
Hg	5461	−0·77	−0·77	±0	Hg	4358	−3·13	−3·13	±0

The calculated values in the above table have been deduced from the equation $\alpha = 0{\cdot}1106/(\lambda^2 - 0{\cdot}1546)$; the systematic deviation from the observed values indicates that a single term equation is no longer sufficient to express the observed dispersion.

Rotatory Power of *d-spiro*-Dihydantoin in Four Equivalents of Aqueous Sodium Hydroxide at 20°.

2·0772 g. hydrated material per 100 c.c.; l = 6 dcm.; $\alpha_{4358}/\alpha_{5461} = 4{\cdot}05$.

λ.	α.	[α].
	°	°
5780	−0·57	− 4·6
5461	−0·78	− 6·3
4358	−3·16	−25·4

1 : 9-*Diacetyl*-l-spiro-5 : 5-*Dihydantoin.*

Anhydrous *l-spiro*-5 : 5-dihydantoin (0·25 gram) is dissolved in the acetic anhydride-pyridine mixture (6 c.c.) and the solution heated at 100–105° for half-an-hour; after cooling, the solvents are distilled off *in vacuo.* The syrupy residue, which crystallises, is dissolved in dry ether, the solution filtered and evaporated *in vacuo*; on treating the residue with warm, dry benzene the pure diacetyl derivative (0·2 gram) is obtained in minute colourless prisms melting at 262–264°. The compound is readily soluble in alcohol, acetone, ether, ethyl acetate, water and chloroform, but almost insoluble in benzene, petroleum ether and carbon tetrachloride ; it crystallises well from acetylene tetrachloride in small prisms. (Found : C = 40·5 ; H = 3·1 per cent. $C_9H_8O_6N_4$ requires C = 40·3 ; H = 3·0 per cent.).

It gave $[\alpha]_{5780}^{13\cdot5^\circ} = -12^\circ$, $[\alpha]_{5461}^{13\cdot5^\circ} = -14^\circ$ in absolute ethyl alcohol and after standing for 3 weeks the solution had $[\alpha]_{5461}^{11^\circ} = -13^\circ$, $[\alpha]_{4358}^{11^\circ} = -23^\circ$ ($l = 2$; $c = 2\cdot039$ g./100 c.c.) ; $[\alpha]_{5780}^{17^\circ} = -32^\circ$, $[\alpha]_{5461}^{17^\circ} = -37^\circ$, $[\alpha]_{4358}^{17^\circ} = -69^\circ$ in water ($l = 2$; $c = 0\cdot8205$ g./100 c.c.), the rotation being unchanged after 40 hours.

After the addition of sodium hydroxide (2 equivalents) to the aqueous solution it gave $[\alpha]_{5780}^{17^\circ} = +7\cdot3^\circ$, $[\alpha]_{5461}^{17^\circ} = +10^\circ$, $[\alpha]_{4358}^{17^\circ} = +25\cdot1^\circ$ ($l = 4$; $c = 0\cdot547$ g./100 c.c.), the rotation being unchanged after standing for 2 weeks.

As in the case of the parent substance, the rotatory power in aqueous solution is changed in sign by the addition of alkali ; this indicates the occurrence of the tautomeric change discussed above and supports Biltz's conclusion that the compound is an N-diacetyl derivative and not an acetic ester.

1 : 9-*Dibenzoyl*-1-spiro-5 : 5-*Dihydantoin*.

The preparation of this substance is similar to that of the racemic isomeride and it crystallises from aqueous acetone in short, colourless needles, which on rapid heating darken at 280° and melt at 307–308° with decomposition. (Found : C = 58·4 ; H = 3·2 per cent. $C_{19}H_{12}O_6N_4$ requires C = 58·2 ; H = 3·1 per cent.). It is readily soluble in acetone, alcohol, ether, ethyl acetate and pyridine and almost insoluble in water, benzene, and chloroform ; it dissolves readily in dilute aqueous soda, ammonia or sodium carbonate.

It had $[\alpha]_{5780}^{12^\circ} = -210^\circ$, $[\alpha]_{5461}^{12^\circ} = -246^\circ$ in ethyl alcohol, ($l = 2$; $c = 1\cdot8595$ g. /100 c.c.), the rotatory power being unchanged after several days.

A solution in dilute aqueous sodium hydroxide (2 equivalents) gave $[\alpha]_{5780}^{17^\circ} = -71^\circ$, $[\alpha]_{5461}^{17^\circ} = -81^\circ$, $[\alpha]_{4358}^{17^\circ} = -160^\circ$ ($l = 2$; $c = 0\cdot2530$ g./100 c.c.), the rotation being unchanged after standing 2 weeks.

A solution in aqueous-alcoholic (60 per cent.) sodium hydroxide (2 equivalents) gave $[\alpha]_{5780}^{17^\circ} = -95^\circ$, $[\alpha]_{5461}^{17^\circ} = -109^\circ$, $[\alpha]_{4358}^{17^\circ} = -215^\circ$ ($l = 4$; $c = 0\cdot5228$ g./100 c.c.).

The very sparing solubility in water of this substance prevents a comparison between its rotatory power in aqueous and alkaline solutions ; the large differences between the specific rotatory powers in alcohol and dilute soda suggest, however, that this compound also undergoes tautomeric change.

The study of the acidic and alkyl derivatives of the optically active *spiro*-dihydantoins is being continued in the expectation that it will yield further results of importance to stereochemistry and the subject of tautomeric change.

Summary.

A carbospirane, *spiro*-5 : 5-dihydantoin, of very simple molecular constitution, has been resolved into optically active components ; it is shown that the externally compensated substance is a racemic compound.

The resolution proceeds in a novel manner in that it involves the separation of mono-brucine *l*-*spiro*-5 : 5-dihydantoin and di-brucine *d*-*spiro*-5 : 5-dihydantoin in the crystalline state.

Determinations of the rotatory dispersion in neutral and alkaline solvents show that the compound exists in two or more tautomeric forms. Evidence of a new type is thus furnished indicating that the molecular component, —NH . CO . NH—, exists in an enolic as well as a ketonic form.

Evidence has been obtained indicating that the 1 : 9-diacidyl-derivatives of the dihydantoin also undergo tautomeric change.

The racemic dihydantoin has an abnormally high density in the crystalline state ; this fact is correlated with its low solubility and high melting point.

The Condensation of Chloral with Urea and Phenyl Urea.

By Frederick Daniel Chattaway, F.R.S., and Eric John Francis James.

(Received August 27, 1931.)

The condensation of chloral with urea was first observed by Jacobsen,* who found that *monochloral urea* $CCl_3 . CH(OH) . NH . CO . NH_2$ (I), and *dichloral urea* $CCl_3 . CH(OH) . NH . CO . NH . CH(OH) . CCl_3$ (II), were respectively produced when excess of urea, or of chloral, was employed. His results were confirmed by Coppin and Titherley,† but otherwise the compounds have been little studied.

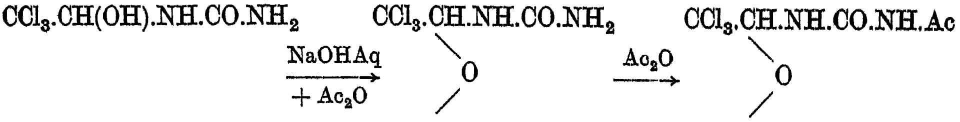
Monochloral urea separates in almost theoretical amount when an aqueous solution of chloral and its equivalent of urea are allowed to stand at the ordinary temperature for several days. Dichloral urea similarly separates when two equivalents of chloral and one equivalent of urea are employed.

Both monochloral urea and dichloral urea are well crystallised, colourless substances, insoluble in water, but soluble in organic solvents. They dissolve in aqueous alkalis, and separate unchanged when such solutions are immediately neutralised, but are hydrolysed when the solutions are kept for any length of time, or are heated, chloroform, urea, and sodium formate being produced. For example, monochloral urea is thus hydrolysed quantitatively when it is dissolved in a warm alcoholic solution of sodium hydroxide.

$$CCl_3 . CH\,(ONa) . NH . CO . NH_2 \xrightarrow{H_2O} CHCl_3 + H . COONa + NH_2CONH_2.$$

When acetic anhydride is added to monochloral urea a *diacetyl derivative* of the constitution $CCl_3 . CH\,(OAc) . NH . CO . NHAc$ is produced.

When, however, acetic anhydride is added to monochloral urea dissolved in a dilute aqueous solution of sodium hydroxide, a remarkable reaction occurs, two molecules of the monochloral urea losing one molecule of water and forming an ether, *bis-(α-carbamido-βββ-trichloroethyl) ether* (III). This is a well-crystallised colourless compound which reacts with acetic anhydride forming a di-acetyl derivative.



I. III.

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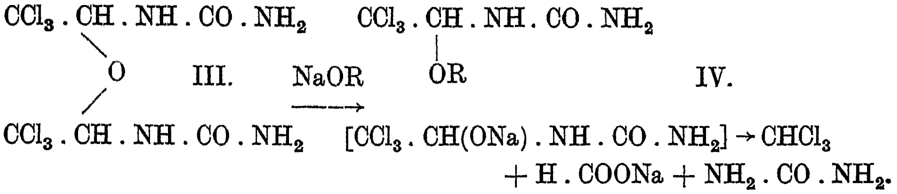
* 'Ann. Chem. Pharm.,' vol. 157, p. 246 (1871).

† 'J. Chem. Soc.,' vol. 105, p. 32 (1914).

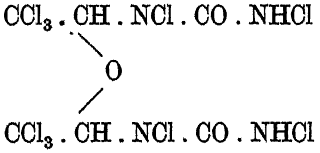
When this ether, dissolved in a solution of any sodium alkoxide in the corresponding alcohol, is allowed to stand for some hours at the ordinary temperature, fission at the ether-linkage occurs, with formation of an *α-alkoxy-βββ-trichloroethyl carbamide* (IV), and of the sodium salt of monochloral urea which then hydrolyses to chloroform, urea, and sodium formate.



$$\left.\begin{array}{l}\mathrm{CCl_3 . CH . NH . CO . NH_2}\\ \mathrm{CCl_3 . CH . NH . CO . NH_2}\end{array}\right\rangle \mathrm{O}\quad \text{III.}\quad \xrightarrow{\mathrm{NaOR}} \begin{array}{l}\mathrm{CCl_3 . \underset{\overset{|}{OR}}{CH} . NH . CO . NH_2}\qquad \text{IV.}\\ \mathrm{[CCl_3 . CH(ONa) . NH . CO . NH_2] \rightarrow CHCl_3}\\ \qquad\qquad\mathrm{+ H . COONa + NH_2 . CO . NH_2.}\end{array}$$

A number of these α-alkoxy-βββ-trichloroethyl carbamides containing the simpler alkyl groups have been prepared. They are all colourless, very well crystallised compounds, which yield with acetic anhydride *monoacetyl derivatives* of the constitution $\mathrm{CCl_3 . CH(OR) . NH . CO . NHAc}$.

When *bis* (α-carbamido-βββ-trichloroethyl) ether (III) is acted upon by chlorine, four of the hydrogen atoms attached to nitrogen are replaced by chlorine, and a substituted nitrogen chloride probably having the constitution



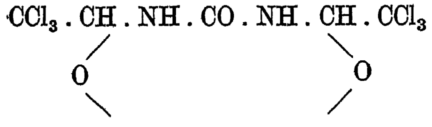
$$\left.\begin{array}{l}\mathrm{CCl_3 . CH . NCl . CO . NHCl}\\ \mathrm{CCl_3 . CH . NCl . CO . NHCl}\end{array}\right\rangle \mathrm{O}$$

is formed.

Dichloral urea (II) when acted upon by acetic anhydride yields a colourless *diacetyl derivative* of the constitution

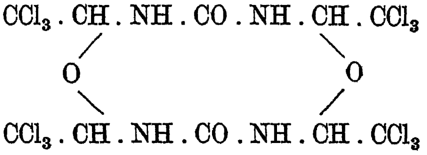
$$\mathrm{CCl_3 . CH(OAc) . NH . CO . NH . CH(OAc) . CCl_3.}$$

When, however, acetic anhydride is added to a dilute alkaline solution of dichloral urea, condensation takes place with loss of water and an anhydro derivative of ether-like structure is formed. This compound has, up to the present, not been obtained in a perfectly pure condition as it does not crystallise well, but it almost certainly has a constitution similar to that of the compound obtained from monochloral urea. It undoubtedly contains the grouping (i) and possibly has the structure (ii)



$$\mathrm{CCl_3 . \underset{\diagup O \diagdown}{CH} . NH . CO . NH . \underset{\diagdown O \diagup}{CH} . CCl_3}$$

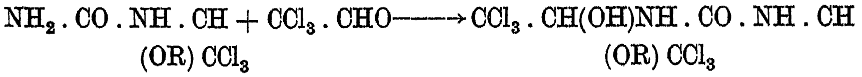
(i)



$$\begin{array}{l}\mathrm{CCl_3 . CH . NH . CO . NH . CH . CCl_3}\\ \qquad\mathrm{O} \qquad\qquad\qquad\qquad\quad \mathrm{O}\\ \mathrm{CCl_3 . CH . NH . CO . NH . CH . CCl_3}\end{array}$$

(ii)

since when it is dissolved in a solution of any sodium alkoxide in the corresponding alcohol, chloroform, urea and sodium formate are produced, together with a *sym-di-(α-alkoxy-βββ-trichloro-ethyl)-carbamide* of the constitution $CCl_3.CH(OR).NH.CO.NH.CH(OR)CCl_3$ (V). A number of these symmetrical di-(α-alkoxy-βββ-trichloroethyl)-carbamides have been prepared. Their constitution is confirmed by their synthesis from the α-alkoxy-βββ-trichloroethyl carbamides (IV). These latter compounds themselves condense with anhydrous chloral and form N-(α-alkoxy-βββ-trichloroethyl)-N′-(α-hydroxy-βββ-trichloroethyl)-carbamides (VI) thus :—



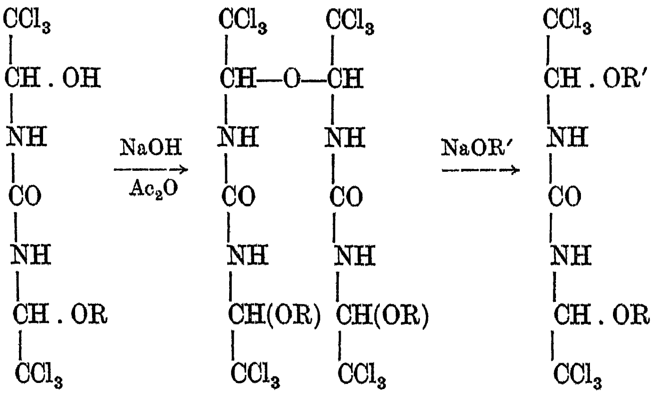
$$NH_2.CO.NH.\underset{(OR)\,CCl_3}{CH} + CCl_3.CHO \longrightarrow CCl_3.CH(OH)NH.CO.NH.\underset{(OR)\,CCl_3}{CH}$$

IV. VI.

These N-(α-alkoxy-βββ-trichloroethyl)-N′-(α-hydroxy-βββ-trichloroethyl) carbamides are also well crystallised, colourless substances, which with acetic anhydride yield monoacetyl derivatives of the structure

$$CCl_3.CH(OAc).NH.CO.NH.CH(OR)CCl_3.$$

They are readily soluble in dilute aqueous alkalis yielding solutions which on addition of acetic anhydride yield *bis-(α-N′-α-alkoxy-βββ-trichloroethyl-carbamido-βββ-trichloroethyl) ethers (VIII)* which themselves, on treatment with a sodium alkoxide dissolved in the corresponding alcohol, yield dialkoxy compounds of the general type $CCl_3.CH(OR).NH.CO.NH.CH(OR').CCl_3$ (VIII), a number of which have been prepared.

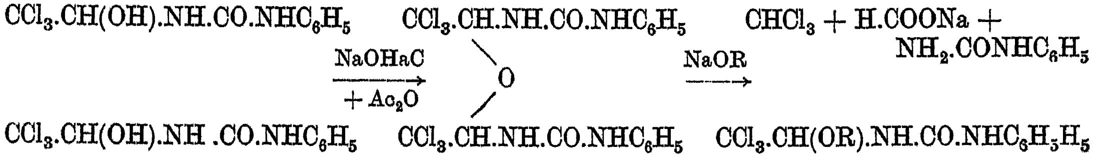


VI. VII. VIII.

The groups R and R′ may be different, or the same, in which case the compounds are identical with those obtained from dichloral urea.

Phenyl urea condenses with chloral in the same way as does urea itself, forming chloral phenyl urea, *N-phenyl-N′-α-hydroxy-βββ-trichloroethyl carbamide* (IX) $CCl_3 . CH(OH)NH . CO . NH . C_6H_5$. Chloral phenyl urea is a colourless, crystalline substance, which forms a colourless *diacetyl derivative* $CCl_3 . CH(OAc) . NH . CO . NAcC_6H_5$ with acetic anhydride. It dissolves readily in dilute aqueous alkalis and separates unchanged if such solutions are immediately neutralised. If such solutions are allowed to stand at the ordinary temperature or are warmed, decomposition takes place with formation of chloroform and some phenyl isocyanide. When acetic anhydride is added to a solution of chloral phenyl urea in dilute aqueous alkali, a similar reaction to that which occurs with monochloral urea takes place, and *bis-(α-N′-phenyl-N-carbamido-βββ-trichloroethyl)-ether is produced* (X). This ether forms a *diacetyl derivative* when acted upon with acetic anhydride, and reacts with alcoholic solutions of sodium alkoxides to form *N-phenyl-N′-(α-alkoxy-βββ-trichloroethyl)-carbamides* of the general formula (XI).

$$CCl_3 . CH(OR) . NH . CO . NH . C_6H_5.$$



$$\begin{array}{ccccc} \mathrm{CCl_3.CH(OH).NH.CO.NHC_6H_5} & & \mathrm{CCl_3.CH.NH.CO.NHC_6H_5} & & \mathrm{CHCl_3 + H.COONa +} \\ & & & & \mathrm{NH_2.CONHC_6H_5} \\ & \xrightarrow[+\,\mathrm{Ac_2O}]{\mathrm{NaOHaC}} & \rangle \mathrm{O} & \xrightarrow{\mathrm{NaOR}} & \\ \mathrm{CCl_3.CH(OH).NH.CO.NHC_6H_5} & & \mathrm{CCl_3.CH.NH.CO.NHC_6H_5} & & \mathrm{CCl_3.CH(OR).NH.CO.NHC_6H_5H_5} \end{array}$$

IX. X. XI.

These α-alkoxy derivatives (XI), a number of which have been prepared, are colourless, well crystallised compounds which with acetic anhydride yield crystalline *monoacetyl derivatives* of the constitution

$$CCl_3 . CH(OR) . NH . CO . N(Ac)C_6H_5.$$

Experimental.

α-hydroxy-βββ-trichloroethyl carbamide (“monochloral urea”)

$$CCl_3 . CH(OH) . NH . CO . NH_2 \text{ (I).}$$

An excess of urea over the equivalent amount is used, as otherwise some dichloral urea is formed.

24 g. of urea (2 mols.) and 33 g. (1 mol.) of chloral hydrate were dissolved in 80 c.c. of water. The solution was at first clear, but after some 12 hours separation of *α-hydroxy-βββ-trichloroethyl carbamide* (I) commenced, and

after 3 days at the ordinary temperature was practically complete. The colourless, crystalline solid was collected, washed with cold water and crystallised from a mixture of alcohol (1 part) and benzene (3 parts) in which it readily dissolved, and from which it separated in compact prisms, m.p. 150° (decomp.).

It is very easily soluble in boiling alcohol, and may be recrystallised from boiling aqueous alcohol, but this solvent is not suitable for obtaining the compound in a pure state, as in presence of water, hydrolysis occurs with liberation of chloral and formation of the more sparingly soluble dichloral urea.

Sym-di-(*α-hydroxy-*ββ β*-trichloroethyl*)*-carbamide* (" dichloral urea ").

$CCl_3 . CH(OH) . NH . CO . NH . CH(OH) . CCl_3$ (II).

12 g. of urea (1 mol.) and 66 g. of chloral hydrate (2 mols.) were dissolved in a mixture of 40 c.c. water and 60 c.c. of concentrated hydrochloric acid, and the solution allowed to stand at the ordinary temperature for 2 days. During this time *sym*-di-(α-hydroxy-βββ-trichloro-ethyl)-carbamide (II) separated almost quantitatively as a bulky, colourless, crystalline solid. This was collected, washed with cold water and crystallised from boiling aqueous alcohol, in which it is easily soluble and from which it separates in colourless, glistening plates, m.p. 194° (decomp.).

Diacetyl monochloral urea, N-(α-acetoxy-βββ-trichloro-ethyl)N′-acetyl carbamide. $CCl_3 . CH(OAc) . NH . CO . NH . Ac$.

5 g. of acetic anhydride (1 mol. and excess) and 1 drop of sulphuric acid were added to 2 g. of monochloral urea. Heat was evolved and on cooling, *diacetyl monochloral urea* separated.

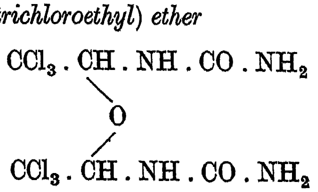
It crystallises from boiling dilute alcohol, in which it is moderately easily soluble, in colourless rhombs, m.p. 160° (decomp.).

(Found: Cl, 36·3; $C_7H_9O_4N_2Cl_3$ requires Cl, 36·5 per cent.)

Diacetyl dichloral urea, sym-di-(α-acetoxy-βββ-trichloro-ethyl) carbamide. $CCl_3 . CH(OAc) . NH . CO . NH . CH(OAc)CCl_3$ which was prepared in a similar way, crystallises from boiling dilute acetic acid, in which it is easily soluble in colourless flattened prisms, m.p. 189° (decomp.).

(Found: Cl, 48·4; $C_9H_{10}O_5N_2Cl_6$ requires Cl, 48·5 per cent.)

Bis-(*α-carbamido-*ββ β*-trichloroethyl*) *ether*



$$\begin{array}{l} CCl_3 . CH . NH . CO . NH_2 \\ \qquad\quad \diagdown \\ \qquad\qquad O \\ \qquad\quad \diagup \\ CCl_3 . CH . NH . CO . NH_2 \end{array}$$

(III).

10 g. of finely powdered monochloral urea were dissolved in 100 c.c. N/1 sodium hydroxide (2 mols.) and 5 g. of acetic anhydride were added, drop by drop, with shaking, the temperature being kept at 0°–5° (20 minutes) *Bis-(α-carbamido-ββ β-trichloroethyl)-ether* (III) separated as a colourless, flocculent solid on each addition of acetic anhydride. It is readily soluble in boiling alcohol and acetic acid, very sparingly soluble in benzene, chloroform or water. It separates from boiling dilute alcohol, in which it is easily soluble in long, slender, colourless, flattened, prisms, m.p. 222° (decomp.). (Found: C, 18·7; H, 2·1; N, 14·0; Cl, 53·4. M (cryoscopic in acetic acid), 375. $C_6H_8N_4O_3Cl_6$ requires C, 18·2; H, 2·0; N, 14·1; Cl, 53·6 per cent; M, 396.)*

It reacts readily with acetic anhydride containing a trace of sulphuric acid, forming bis-(α-N′-acetyl-carbamido-βββ-trichloroethyl)-ether, which crystallises from boiling dilute acetic acid, in which it is moderately soluble in well-formed, colourless, rhombs, m.p. 241° (decomp.).

(Found: Cl, 43·95; $C_{10}H_{12}N_4O_5Cl_6$ requires Cl, 44·25 per cent.)

α-ethoxy-βββ-trichloroethyl-carbamide (IV).

$$CCl_3 . CH(OC_2H_5) . NH . CO . NH_2.$$

5 g. of bis-(α-carbamido-βββ-trichloroethyl) ether (III) were dissolved in 30 c.c. ethyl alcohol, and a solution of 0·3 g. sodium (1 mol.) in 15 c.c. of alcohol was added. The mixture was allowed to stand at the ordinary temperature for 24 hours during which time sodium formate (0·7 g. 80 per cent. theoretical) gradually separated. The filtrate which smelt strongly of chloroform, was poured into 200 c.c. of cold water, when *α-ethoxy-βββ-trichloroethyl carbamide*, IV, separated as a bulky, colourless, crystalline solid. It dissolved easily in boiling dilute alcohol (1 : 1) and separates in long, slender, colourless, flattened prisms, m.p. 202° (decomp.).

(Found: Cl, 45·1; $C_5H_9O_2N_2Cl_3$ requires Cl, 45·2 per cent.)

In a similar way, using the appropriate alcohol and sodium alkoxide, the following compounds were prepared. They all crystallise from boiling aqueous alcohol in which they are easily soluble, in long, slender, colourless flattened prisms.

α-methoxy-βββ-trichloroethyl carbamide $CCl_3 . CH(OCH_3) . NH . CO . NH_2$, m.p. 205° (decomp.).

(Found: Cl, 47·8; $C_4H_7O_2N_2Cl_3$ requires Cl, 48·1 per cent.)

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* Benzoyl chloride may be used for this preparation in place of acetic anhydride, but the product is not so easily obtained pure.

α-n-propoxy-βββ-trichloroethyl-carbamide. $CCl_3.CH(OC_3H_7).NH.CO.NH_2$, m.p., 177° (decomp.). (Found: C, 42·6; $C_6H_{11}O_2N_2Cl_3$ requires Cl, 42·7 per cent.)

α-iso-propoxy-βββ-trichloroethyl-carbamide.

$$CCl_3 . CH(OCH . (CH_3)_2) . NH . CO . NH,$$

m.p., 180° (decomp.). (Found: Cl, 42·5; $C_6H_{11}O_2N_2Cl_3$ requires Cl, 42·7 per cent.)

α-n-butoxy-βββ-trichloroethyl-carbamide. $CCl_3 . CH(OC_4H_9) . NH . CO . NH_2$, m.p., 165° (decomp.). (Found: Cl, 40·4; $C_7H_{13}O_2N_2Cl_3$ requires Cl, 40·4 per cent.)

When warmed with acetic anhydride containing a trace of sulphuric acid, these α-alkoxy-βββ-trichloroethyl carbamides (IV) yield the corresponding N-acetyl compounds, which crystallise well from boiling aqueous alcohol.

N-acetyl-N′-α-methoxy-βββ-trichloroethyl-carbamide.

$$CCl_3 . CH(OCH_3) . NH . CO . NH . Ac,$$

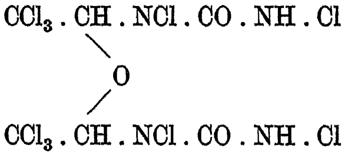
colourless, hexagonal plates, m.p., 154° (decomp.). (Found: Cl, 40·2; $C_6H_9N_2O_3Cl_3$ requires Cl, 40·4 per cent.)

N-acetyl-N′-α-ethoxy-βββ-trichloroethyl-carbamide.

$$CCl_3 . CH(OC_2H_5) . NH . CO . NH . Ac,$$

long, slender, colourless flattened prisms, m.p. 142° (decomp.). (Found: Cl, 38·1; $C_7H_{11}N_2O_3Cl_3$ requires Cl, 38·35 per cent.)

Bis-(α-NN′-dichlorocarbamido-βββ-trichloroethyl)-ether.



5 g. of *bis*-(α-carbamido-βββ-trichloroethyl)-ether were dissolved in small portions at a time in 50 c.c. of glacial acetic acid, the liquid being saturated with chlorine after each addition. The liquid was then poured over crushed ice when *bis-(α-NN′-dichloro carbamido-βββ-trichloroethyl) ether* separated as a granular solid. It was crystallised from warm acetic acid, saturated with chlorine, in which it is easily soluble, and from which it separates in clusters of colourless, compact, prisms, m.p., 131° (decomp. with slight explosion).

(Found: Cl as N-Cl, 26·2; total Cl, 66·0; $C_6H_4N_4O_3Cl_{10}$ requires Cl as N-Cl, 26·5; total Cl, 66·3 per cent.)

Anhydro Dichloral Urea.—5 g. of dichloral urea were dissolved in 28·2 c.c. ice cold N/1 sodium hydroxide (2 mols.) and 2·5 g. of acetic anhydride (1 mol.) were added drop by drop with shaking, the temperature being kept at 0°–5°. At each addition of acetic anhydride, *anhydro dichloral urea* separated as a colourless, flocculent, solid, which, when all the acetic anhydride had been added, was collected, washed with cold water, and dried at 50°. The melting point of the crude, dry, substance was 137°.*

This substance was found to be extremely difficult to obtain in a crystalline state. It is very soluble in all ordinary organic solvents, except petroleum, ether and water, and does not separate even from strong solutions on cooling. When any attempt is made to crystallise it from mixed solvents it separates as liquid droplets which only slowly solidify. The results of analyses of this compound are therefore unreliable, and evidence for its constitution is obtained only from its reaction with sodium ethoxide.

Sym-di-(α-ethoxy-βββ-trichloroethyl) carbamide.

$$CCl_3 . CH(OC_2H_5)NH . CO . NH . CH(OC_2H_5) . CCl_3 \quad (V).$$

5 g. anhydro dichloral urea were dissolved in 20 c.c. of ethyl alcohol and 0·3 g. sodium dissolved in 30 c.c. alcohol added. The mixture was left for 12 hours, during which time sodium formate separated, and then poured into 100 c.c. of cold water, when *sym-di-(α-ethoxy-βββ-trichloro-ethyl)-carbamide* separated as a colourless, finely divided, crystalline solid. It was crystallised repeatedly from boiling alcohol, diluted with half its bulk of water, in which it is moderately soluble, and from which it separates in long, slender, colourless, flattened prisms, m.p., 241° (decomp.). (Found: Cl, 51·8; N, 6·6; $C_9H_{14}O_3N_2Cl_6$ requires Cl, 51·8; N, 6·8 per cent.)

It is readily soluble in most organic solvents. When added to acetic anhydride containing a trace of sulphuric acid no heat was developed, and on adding water the compound was recovered unchanged.

In a similar way the following members of the series were prepared. They crystallise from boiling aqueous alcohol, in which they are moderately soluble, in long, slender, colourless, flattened prisms. *Sym-di-(α-methoxy-βββ-trichloroethyl)-carbamide.* $CCl_3 . CH(OCH_3) . NH . CO . NH . CH(OCH_3) . CCl_3$, m.p., 234° (decomp.). (Found: Cl, 55·3; N, 7·0; $C_7H_{10}O_3N_2Cl_6$ requires Cl, 55·6; N, 7·3 per cent.)

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* *Cf.* Feist, 'Ber. Deuts. Chem. Ges.,' vol. 47, p. 1189 (1914).

Sym-di-(α-n-propoxy-βββ-trichloroethyl)-carbamide.

$$CCl_3 . CH(OC_3H_7) . NH . CO . NH . CH(OC_3H_7) . CCl_3,$$

m.p., 224° (decomp.). (Found: Cl, 48·2; $C_{11}H_{18}O_3N_2Cl_6$ requires Cl, 48·5 per cent.)

N(α-ethoxy-βββ-trichloroethyl)N′(α-hydroxy-βββ-trichloroethyl)-carbamide.

$$CCl_3 . CH(OC_2H_5)NH . CO . NH . CH(OH) . CCl_3 \quad (VI).$$

5 g. α-ethoxy-βββ-trichloroethyl carbamide, were added to 10 g. (excess) of anhydrous chloral, and the mixture warmed on the water-bath for about half an hour until a clear viscid liquid was obtained. 100 c.c. water were then added and the whole vigorously stirred, when *N(α-ethoxy-βββ-trichloroethyl)-N′(α-hydroxy-βββ-trichloroethyl)-carbamide* separated as a flocculent solid which quickly became granular. It was crystallised several times from boiling aqueous alcohol, in which it is readily soluble and from which it separates in long, slender, colourless, flattened prisms, m.p., 147° (decomp.). (Found: Cl, 55·2; $C_7H_{10}O_3N_2Cl_6$ requires Cl, 55·6 per cent.)

It dissolves readily in dilute alkalis, giving solutions which if kept for a few hours decompose, liberating α-ethoxy-βββ-trichloroethyl carbamide (IV) as a colourless crystalline solid, the chloral formed at the same time breaking down to chloroform and formate.

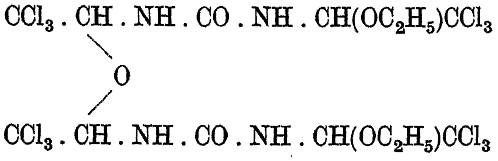
N(α-methoxy-βββ-trichloroethyl)-N′-(α-hydroxy-βββ-trichloroethyl) carbamide prepared in a similar way from α-methoxy-βββ-trichloroethyl carbamide separated from boiling aqueous alcohol in which it is readily soluble in clusters of long, slender, colourless, flattened prisms, m.p., 159° (decomp.). (Found: Cl, 57·8; $C_6H_8O_3N_2Cl_6$ requires 57·8 per cent.)

Both these compounds, when warmed with acetic anhydride containing a trace of sulphuric acid yielded monoacetyl derivatives.

N(α-ethoxy-βββ-trichloroethyl)-N′-(α-acetoxy-βββ-trichloroethyl) carbamide. $CCl_3 . CH(OC_2H_5)NH . CO . NH . CH(OAc) . CCl_3$, colourless, flattened, prisms from dilute alcohol, m.p., 187° (decomp.). (Found: Cl, 49·8; $C_9H_{12}O_4N_2Cl_6$ requires Cl, 50·1 per cent.)

N(α-methoxy-βββ-trichloroethyl)-N′-(α-acetoxy-βββ-trichloroethyl) carbamide. $CCl_3 . CH(OCH_3) . NH . CO . NH . CH(OAc) . CCl_3$, colourless, flattened, prisms from dilute acetic acid, m.p., 189° (decomp.). (Found: Cl, 51·4; $C_8H_{10}O_4N_2Cl_6$ required Cl, 51·8 per cent.)

Bis-[*α-*(*N′-α-ethoxy-*βββ*-trichloroethyl-carbamido*)*-*βββ*-trichloroethyl*] *ether.*



$$\begin{array}{l} \mathrm{CCl_3\,.\,CH\,.\,NH\,.\,CO\,.\,NH\,.\,CH(OC_2H_5)CCl_3} \\ \qquad\quad\diagdown \\ \qquad\qquad \mathrm{O} \\ \qquad\quad\diagup \\ \mathrm{CCl_3\,.\,CH\,.\,NH\,.\,CO\,.\,NH\,.\,CH(OC_2H_5)CCl_3} \end{array}$$

(VII).

3 g. N (α - ethoxy - βββ-trichloroethyl) - N′- (α-hydroxy - βββ - trichloroethyl) - carbamide (VI) were dissolved in 15 c.c. N/1 sodium hydroxide and 1 g. acetic anhydride added, drop by drop, with shaking, the liquid being kept at 0°–5°, when a colourless, flocculent solid separated. This was collected, washed, and cautiously dried. It is very soluble in all ordinary organic solvents, and from aqueous solvents it separates in oily droplets. As it could not be obtained crystalline, the analytical data are not trustworthy, but from its reaction with sodium ethoxide, the compound is certainly *bis-*(*α-N′-α-ethoxy-*βββ*-trichloroethyl-carbamido-*βββ*-trichloroethyl*)*-ether,* VII.

Sym-di-(*α-ethoxy-*βββ*-trichloroethyl*)*-carbamide.*

$$\mathrm{CCl_3\,.\,CH(OC_2H_5)NH\,.\,CO\,.\,NH\,.\,CH(OC_2H_5)CCl_3} \quad \mathrm{(V).}$$

2·5 g. of *bis* [(*α-*(*N′-α-ethoxy-*βββ*-trichloroethyl-carbamido*)*-*βββ*-trichloroethyl*)] *ether* (VII) were dissolved in 15 c.c. ethyl alcohol and a solution of 0·2 g. sodium in 20 c.c. alcohol added. The mixture was allowed to stand at the ordinary temperature for 12 hours and was then poured into 100 c.c. of cold water, when *sym-di-*(*α-ethoxy-*βββ*-trichloroethyl*)*-carbamide* (V) separated. It crystallises from boiling dilute alcohol, in which it is easily soluble, in long, slender, colourless, flattened prisms, m.p., 241° (decomp.) identical in every way with that prepared by the action of sodium ethoxide on anhydro dichloral urea.

The following compounds were similarly prepared using solutions of sodium in the appropriate alcohols. They crystallise from boiling aqueous alcohol, in which they are moderately soluble, in long, slender, colourless, flattened prisms.

N-(*α-ethoxy-*βββ*-trichloroethyl*) *- N′-* (*α-methoxy-*βββ*-trichloroethyl*) *carbamide.* $\mathrm{CCl_3\,.\,CH(OC_2H_5)\,.\,NH\,.\,CO\,.\,NH\,.\,CH(OCH_3)\,.\,CCl_3}$, m.p., 212° (decomp.). (Found: Cl, 53·9; $\mathrm{C_8H_{12}O_3N_2Cl_6}$ requires Cl, 53·6 per cent.)

N-(*α-ethoxy-*βββ*-trichloroethyl*)*-N′-*(*α-n-propoxy-*βββ*-trichloroethyl*) *carbamide.* $\mathrm{CCl_3\,.\,CH(OC_2H_5)\,.\,NH\,.\,CO\,.\,NH\,.\,CH(OC_3H_7)\,.\,CCl_3}$, m.p., 228° (decomp.). (Found: Cl, 49·7; $\mathrm{C_{10}H_{16}O_3N_2Cl_6}$ requires Cl, 50·1 per cent.)

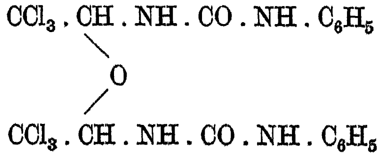
Chloral Phenyl Urea.—$\mathrm{CCl_3\,.\,CH(OH)\,.\,NH\,.\,CO\,.\,NH\,.\,C_6H_5}$ (IX).

13·2 g. of phenyl urea and 40 g. of chloral hydrate (2½ mols.) were dissolved in a mixture of 40 c.c. of water and 50 c.c. concentrated hydrochloric acid. A clear solution was obtained, from which, on standing, *N-phenyl-N'-α-hydroxy-βββ-trichloroethyl carbamide* separated as a colourless, crystalline solid. After 2 days it was collected, washed with cold water, and crystallised from boiling aqueous alcohol in which it is readily soluble and from which it separated in slender, colourless, flattened prisms, m.p., 142° (decomp.). Yield 23 g. (Found: Cl, 37·3; $C_9H_9N_2O_2Cl_3$ requires Cl, 37·5 per cent.)

It is very soluble in alcohol and in acetic acid; sparingly soluble in benzene or chloroform, and practically insoluble in water. It dissolves readily in dilute alkalis, the solution decomposing on standing or warming, some phenyl isocyanide being formed.

With acetic anhydride containing a trace of sulphuric acid it forms *diacetyl chloral phenyl urea.* $CCl_3 . CH(OAc) . NH . CO . NAc . C_6H_5$ which crystallises from boiling dilute acetic acid, in which it is moderately soluble in clusters of small compact prisms, m.p., 104° (decomp.). (Found: Cl, 28·7; $C_{13}H_{13}O_4N_2Cl_3$ requires Cl, 29·0 per cent.)

Bis-(α-N'-phenyl carbamido-βββ-trichloroethyl)-ether.



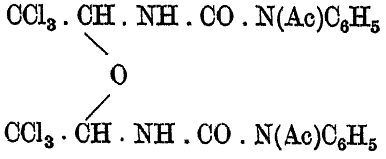
$$\begin{array}{l} CCl_3\,.\,CH\,.\,NH\,.\,CO\,.\,NH\,.\,C_6H_5 \\ \qquad\diagdown \\ \qquad\ \ O \\ \qquad / \\ CCl_3\,.\,CH\,.\,NH\,.\,CO\,.\,NH\,.\,C_6H_5 \end{array}$$

(X).

14 g. of chloral phenyl urea (IX) were dissolved in 100 c.c. of ice cold N/1 sodium hydroxide, and 5 g. of acetic anhydride were added with constant shaking, the temperature being maintained at 0°–5°.

Bis-(α-N'-phenyl-carbamido-βββ-trichloroethyl)-ether (X) separates as a bulky, colourless solid. It crystallises from boiling dilute acetic acid in which it is moderately easily soluble in colourless, compact, four-sided prisms, which on heating begin to soften and decompose at about 195° and finally melt with complete decomposition at 236°. (Found: C, 38·95; H, 3·1; N, 9·9; Cl, 38·4; $C_{18}H_{16}O_3N_4Cl_6$ requires C, 39·3; H, 2·9; N, 10·1; Cl, 38·8 per cent.). It is a well-crystallised substance, readily soluble in alcohol and acetic acid, sparingly soluble in benzene and chloroform, and almost insoluble in water.

With acetic anhydride containing a trace of sulphuric acid it forms *bis-(α-N'-phenyl-N'-acetyl-carbamido βββ-trichloroethyl)-ether*



$$\begin{array}{l} CCl_3\,.\,CH\,.\,NH\,.\,CO\,.\,N(Ac)C_6H_5 \\ \qquad\diagdown \\ \qquad\ \ O \\ \qquad / \\ CCl_3\,.\,CH\,.\,NH\,.\,CO\,.\,N(Ac)C_6H_5 \end{array}$$

colourless rhombs, m.p., 153° (decomp.) from dilute acetic acid. (Found: Cl, 33·8; $C_{22}H_{20}N_4O_5Cl_6$ requires Cl, 33·7 per cent.)

N-phenyl-N′-(α-ethoxy-βββ-trichloroethyl)-carbamide.

$$CCl_3 . CH(OC_2H_5)NH . CO . NH . C_6H_5 \text{ (XI)}.$$

5 g. of *bis*-(α-N′-phenyl-carbamido-βββ-trichloroethyl)-ether (X) were dissolved in 20 c.c. ethyl alcohol and a solution of 0·2 g. sodium in 20 c.c. ethyl alcohol was added. The mixture was allowed to stand at the ordinary temperature for 12 hours, during which time sodium formate separated, and was then poured into 200 c.c. water, when *N-phenyl-N′-α-ethoxy-βββ-trichloroethyl carbamide* separated as a colourless crystalline solid. It crystallises from boiling aqueous alcohol, in which it is moderately soluble, in long, slender, colourless, flattened prisms, m.p., 153° (decomp.). (Found: Cl, 34·2; $C_{11}H_{13}N_2O_3Cl_3$ requires Cl, 34·2 per cent.)

N-phenyl-N′-α-methoxy-βββ-trichloroethyl-carbamide.

$$CCl_3 . CH(OCH_3)NH . CO . NH . C_6H_5,$$

prepared in a similar way, crystallises from boiling aqueous alcohol, in which it is moderately soluble, in long, slender, colourless, flattened prisms, m.p., 189° (decomp.). (Found: Cl, 35·65; $C_{10}H_{11}N_2O_3Cl_3$ requires Cl, 35·8 per cent.) Both of these compounds yielded monoacetyl derivatives when added to acetic anhydride containing a trace of sulphuric acid.

N-phenyl-N-acetyl-N′-(α-ethoxy-βββ-trichloroethyl)-carbamide.

$$CCl_3 . CH(OC_2H_5)NH . CO . N(Ac)C_6H_5,$$

long, colourless prisms from dilute alcohol, m.p., 88° (decomp.). (Found: Cl, 29·6; $C_{13}H_{15}N_2O_3Cl_3$ requires Cl, 30·1 per cent.)

N-phenyl-N-acetyl-N′-(α-methoxy-βββ-trichloroethyl)-carbamide.

$$CCl_3 . CH(OCH_3) . NH . CO . N(Ac)C_6H_5,$$

clusters of colourless prisms from dilute alcohol, m.p., 102° (decomp.). (Found: Cl, 31·0; $C_{12}H_{13}N_2O_3Cl_3$ requires Cl, 31·3 per cent.)

Summary.

In aqueous solution, urea condenses with 1 or 2 molecules of chloral yielding *monochloral-urea* $CCl_3 . CH(OH) . NH . CO . NH_2$ and *dichloral urea* $CCl_3 . CH(OH) . NH . CO . NH . CH(OH)CCl_3$ respectively.

When monochloral urea is treated in dilute alkaline solution with acetic anhydride, 2 molecules condense with the elimination of a molecule of water, and an ether bis-(α-carbamido-βββ-trichloroethyl)-ether is formed.

When this is allowed to stand in an alcoholic solution of the corresponding sodium alkoxide, sodium formate, chloroform and urea are formed together with an *α-alkoxy-βββ-trichloroethyl-carbamide* of the general formula $CCl_3 . CH(OR) . NH . CO . NH_2$.

Dichloral urea resembles monochloral urea in its reactions. Thus, when acetic anhydride is added to its solution in dilute alkali, an *anhydrodichloral urea* is formed, which when treated with a solution of any sodium alkoxide in the appropriate alcohol yields a *sym-NN′-(α-alkoxy-βββ-trichloroethyl)-carbamide* of the general formula $CCl_3CH(OR)NH . CO . NHCH(OR)CCl_3$.

The α-alkoxy-βββ-trichloroethyl-carbamides themselves condense with anhydrous chloral to yield *N-(α-alkoxy-βββ-trichloroethyl)-N′-(α-hydroxy-βββ-trichloroethyl)-carbamides* of the type

$$CCl_3 . CH . OR . NH . CO . NH . CH . OH . CCl_3.$$

These, when treated with acetic anhydride in dilute solution, yield *anhydro compounds* which when acted upon by any sodium alkoxide dissolved in the corresponding alcohol yield ethers of the general formula

$$CCl_3 . CH . OR . NH . CO . NH . CH . OR' . CCl_3.$$

Chloral also condenses similarly with phenyl urea yielding *chloral phenyl urea* $CCl_3 . CH(OH) . NH . CO . NH . C_6H_5$.

Chloral phenyl urea when acted upon in dilute alkaline solution with acetic anhydride, loses water and forms *anhydro-chloral phenyl urea*, and this when treated with any sodium alkoxide dissolved in the corresponding alcohol, forms an *N-phenyl-N′-(α-alkoxy-βββ-trichloroethyl)-carbamide* of the general formula $CCl_3 . CH(OR) . NH . CO . NH . C_6H_5$.

An Investigation of the Attack of Platinum and Tungsten by Iodine.

By Gordon Van Praagh and Eric Keightley Rideal, F.R.S.

(Received September 18, 1931.)

The reactions which are most likely to prove fruitful in elucidating the mechanism of heterogeneous gas reactions are those involving gases having a simple molecular structure, and an investigation was therefore begun by studying the attack of platinum by oxygen at low pressures, as reported in a previous communication.* These investigations have now been extended to the reactions of platinum and tungsten with iodine vapour at low pressures. A marked difference in the behaviour of the two metals was to be anticipated from several considerations, firstly, tungsten is much more readily attacked by oxygen than is platinum, and secondly, the effect of iodine on the thermionic emission is different for the two metals. Kalandyk† observed that the emission from platinum was greatly enhanced by iodine vapour, whereas Langmuir‡ found that iodine had no influence on the emission from tungsten.

The difference in the case of oxidation was accounted for in terms of the large difference in the work functions of the two metals. The thermionic data show that the adsorption of iodine on platinum is stronger than on tungsten, and this can also be ascribed to the difference in the work functions.

Towards iodine the metals were found to behave in a manner to be expected from this difference in work function, for, at low temperatures, the tungsten was attacked by the molecular iodine, and the platinum was not; at high temperatures, dissociation of the iodine into atoms occurred on the platinum more readily than on the tungsten, owing to the stronger adsorption of the gas on the former metal; and finally, attack of the tungsten by atomic iodine took place much more readily than that of platinum.

A distinction between the various possible modes of these heterogeneous actions can also be made by comparing the observed rates of reaction with those calculated on the assumptions involved in the different hypothetical cases.

(*a*) *The Attack of Platinum by Iodine—Experimental.*

The apparatus used was similar to that employed by Langmuir in his studies of chemical reactions at low pressures. The platinum was in the form of a filament, about 16 cm. long and 0·007 cm. in diameter. It was welded to platinum leads, 0·07 cm. in diameter, sealed through the glass of the reaction vessel. This consisted of a cylindrical bulb of about 60 c.c. capacity connected directly to a Pirani gauge. The gauge and reaction vessel were evacuated simultaneously by a mercury diffusion pump, backed by a " Hyvac " pump, through phosphorus pentoxide drying tubes, and cadmium and liquid air traps to exclude mercury vapour. Each new reaction vessel was baked out in an electric furnace at 300° C., for 2 hours or so, a vacuum of 10^{-5} mm. Hg being maintained to remove gases and water vapour.

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* Rideal and Wansbrough-Jones, 'Proc. Roy. Soc.,' A, vol. 123, p. 214 (1929).

† 'J. Phys. Rad.,' vol. 9, p. 231 (1928).

‡ Private communication.

The iodine was recrystallised from potassium iodide and then sublimed several times *in vacuo* in the apparatus. Its vapour pressure at 0° C., as measured on the Pirani gauge, remained the same over a period of a year, which is good evidence for its purity. The iodine reservoir remained evacuated throughout the experiments.

Low vapour-pressure grease, supplied by Metropolitan Vickers Company, was used to lubricate the glass taps, and apart from an initial attack by the iodine, no noticeable liberation of volatile products of interaction was observed over long periods of time.

The Pirani gauge consisted of a fine platinum wire, about 30 cm. long, sealed into a cylindrical glass vessel of about 50 c.c. capacity. The wire was heated to about 100° C. by a 2-volt accumulator. The gauge was used in the method recommended by Campbell,* in which the voltage required to keep the filament at a constant temperature (as indicated by its resistance measured by a Wheatstone bridge circuit) is measured. It was calibrated against the vapour pressure of iodine at temperatures from 0° to —40° C., utilising the data summarised in the International Critical Tables (Crommelin, Onnes, Ramsay, Travers). It was found that the expression $V^2 - V_0^2/V_0^2$, where V_0 is the voltage required to maintain the wire *in vacuo* at some arbitrary temperature and V the voltage required at pressure p, was proportional to the pressure over the range of the experiments, viz., 0·03 to 0·0001 mm. Hg. The voltage was measured by a millivoltmeter, and the pressure could easily be ascertained to 0·0001 mm. of Hg. A check at the conclusion of the experiments showed no variation from the original calibration.

The platinum filament was heated by 16-volt accumulators and was " out-gassed " by heating at about 1300° C. for about 8–12 hours in a good vacuum. It formed one arm of a Wheatstone bridge circuit, and the temperature was measured in terms of the resistance of the wire compared with a standard, using 10,000 ohms in the ratio arms. The standard consisted of a coil of constantan wire in insulating oil in an ice-bath. The oil was stirred by a current of dry air and it was considered that the resistance of this standard remained constant throughout the experiments.

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* ' Proc. Phys. Soc.,' vol. 33, p. 287 (1921).

By maintaining the resistance of the filament constant during a run, the temperature was kept constant, as it was found that the change in resistance due to thinning of the wire was negligible during any one run. The temperature was calculated from the resistance-temperature data for platinum, and checked by an optical pyrometer, which had been previously calibrated by comparison with an incandescent platinum strip, upon which substances of different known melting points were placed. The resistance of the wire (less that of the leads) was measured at 0° C. between several runs. It was found that this zero resistance increased by 0·3 per cent. for every run. This agreed with the change calculated from the quantity of platinum removed as iodide by the reaction. The measured resistance at the higher temperature was corrected for cooling by the leads, using the method given by Langmuir.* The temperature was then found from a graph of the expression

$$\mathrm{R}t/\mathrm{R}_0 = (1 + 0{\cdot}00398t - 0{\cdot}00000058t^2),$$

using the corrected value of Rt and the appropriate value of R_0.

In all runs, the vapour pressure of iodine at 0° C. was used as the initial pressure and the runs were continued till the pressure fell to $1{\cdot}0 \times 10^{-4}$ mm. The reaction vessel and Pirani gauge were surrounded by an ice-bath.

Experimental Results.

Dissociation of Iodine into Atoms.—At filament temperatures from 270° K. to 1200° K. no change in pressure of the iodine vapour could be observed, apart from a small initial fall due to adsorption of the iodine on the glass walls of the vessel.†

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* Langmuir, MacLane and Miss Blodgett, 'Phys. Rev.,' vol. 35, p. 478 (1930).

† In order to investigate how large a correction might be necessary for desorption, during a run, of the iodine adsorbed on the walls at the beginning of a run, experiments were performed to measure the quantity of iodine desorbed when the pressure was dropped from its initial value of p_0 to various values of p.

If Z be the pressure to be deducted from p at any given time to give the true value, K_1 and K_2 be proportional to the velocity constants of the rate of adsorption and desorption respectively, then, if the initial quantity adsorbed be p_0' at a pressure p_0 and $p = f(t)$ represents the experimental p, t curves

$$\mathrm{Z} = \mathrm{K}_2 p_0' e^{-\int[\mathrm{K}_2+\mathrm{K}_1 f(t)]\,dt} \int e^{\int[\mathrm{K}_2+\mathrm{K}_1 f(t)]\,dt}\, dt.$$

(See Van Praagh and Pringle, 'Proc. Camb. Phil. Soc.,' vol. 27, ii, p. 250 (1931).)

The correction was applied to four runs and, although in extreme cases p_0' was as high as 10 per cent. of p_0, yet the change in dp/dt at various times was negligible.

On raising the filament temperature to 1300° K. a gradual diminution of the iodine pressure was obtained, which eventually fell to zero. On admitting a second charge of iodine vapour (at 0·027 mm. Hg) the pressure again fell to zero, but in the third run the pressure began to rise instead of fall, and in the fourth run the pressure rose to about 3/2 of its initial value.

The walls of the reaction vessel were then heated to about 200° C., and on cooling to 0° C. the experiment was repeated, when it was found that the pressure fell as in the first experiment. Again, after two runs the pressure rose, but the rates of clean up were perfectly reproducible provided that the vessel was heated between each run.

On contact with the hot wire the iodine is partly dissociated into atoms, and the atoms are strongly adsorbed on to the glass wall, thus causing a fall in pressure. Since the initial pressure of the iodine was 0·027 mm. Hg and the volume of the vessel and Pirani gauge 120 c.c. after two runs $5 \cdot 10^{17}$ iodine atoms have been removed by adsorption. The area of the glass walls of the reaction vessel was about 70 sq. cm. At the beginning of the third run, therefore, if the area of an iodine atom be taken at $5 \cdot 3$ $\text{A}^{\circ 2}$ and if the specific surface of the glass were about three and a half times the superficial area, there would be approximately a unimolecular layer of atoms on the surface. When the glass surface is saturated, on further formation of atoms the pressure rises until, apart from a slow rate of attack of the wire by the iodine atoms, an almost stationary state between dissociation and recombination is attained. Heating the glass to 200° C. effects the recombination of the adsorbed atoms and their liberation as molecules. The iodine atoms adsorbed on the glass evaporated as molecules after several hours at room temperature. A pressure reading taken on the morning after a run had been done, showed that the initial pressure had been built up again, *i.e.*, all the iodine atoms had been desorbed.

The energy of activation for the process of dissociation of molecular iodine on platinum can be determined approximately from the rates of fall of pressure at different temperatures by means of the Arrhenius equation

$$Q = RT^2 \frac{d \log k}{dT},$$

where k is the velocity constant for the rate of dissociation at temperature T. The data for a few of the experimental runs showing the change of pressure with time are given in the tables.

Experiment 18. T = 1297° K.

t (minutes).	p (mm. Hg).	t (minutes).	p (mm. Hg).
5	0·0247	30	0·0139
10	0·0224	35	0·0123
15	0·0202	40	0·0110
20	0·0181	45	0·0098
25	0·0160		

Experiment 24. T = 1345° K.

t (minutes).	p (mm. Hg).	t (minutes).	p (mm. Hg).
5	0·0205	30	0·0050
10	0·0168	35	0·0034
15	0·0129	40	0·0020
20	0·0100	45	0·0012
25	0·0077		

From these data the values of $dp/dt/p$ (which is equal to the velocity constant k) can be obtained, and the heat of dissociation can be calculated from the Arrhenius equation. This is at the best only very approximate since the $dp/dt - p$ curves are only linear in the initial stages and at low temperatures, indicating that in general the removal of iodine atoms by adsorption on the glass walls of the vessel is not equal to their rate of formation at the surface of the hot wire.

A specimen value obtained from the initial stages of the runs is given below :—

Experiment number.	Temp. (° K.).	$dp/dt/p$ (k) (seconds).	$\log_e k$.	Q (cals. per gram.-mol.).
22	1297	0·00017	−8·680	41,700
25	1345	0·00030	−8·112	

An attempt was made to determine the energy change involved in dissociation by another method, similar to that adopted by Langmuir* for determining the heat of dissociation of hydrogen. Measurements were made of the excess energy required to maintain the temperature of the wire at some fixed value in iodine vapour at a known pressure, above that required to maintain it at the same temperature *in vacuo*. This excess energy is removed (1) by convection by the iodine and (2) by the dissociation process. The energy removed by convection was found at temperatures below those at which dissociation occurred, and the energy used in the dissociation process was then found by difference. The differences, however, were small, and difficult to measure accurately. This presumably accounts for the fact that the heat conducted away was constant over a range of filament temperatures of from 1220° to 1297° K., whereas it should be proportional to the excess temperature of the filament over the surroundings.

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* 'J. Amer. Chem. Soc.,' vol. 34, p. 860 (1912).

The data obtained at a pressure of 0·027 mm. Hg are given below :—

Temperature (° K.).	Watts consumed in iodine less that *in vacuo*.	Watts consumed in the dissociation process.
1220	0·0794	0
1247	0·0800	0
1274	0·0794	0
1297	0·0870	0·007
1321	0·1028	0·023
1345	0·1147	0·035
1395	0·1366	0·057
1419	0·1506	0·071

The watts consumed were obtained from the ammeter readings and the resistance of the wire, corrected for cooling by the leads and for their resistance. To obtain the figures in the last column, 0·08 watts was taken as the heat removed by convection and subtracted from the figures in the second column.

The temperature of the molecules striking the wire cannot have been far removed from that of the walls of the vessel, since on heating the wire below reaction temperatures, no appreciable rise in pressure was observed. Since the mean free path of the gas molecules at 0·027 mm. Hg is about 1·5 mm., it is unlikely that there is an equilibrium between molecules and atoms in a zone round the wire such as would be expected at higher pressures. Consequently, the process can be regarded as the dissociation of a certain fraction of the molecules which hit the wire. If n is the number of molecules dissociating per second, and E the energy of activation for the process on which the temperature coefficient is dependent, then, from the Arrhenius equation

$$\log k = \log n = -\frac{\mathrm{E}}{\mathrm{RT}} + \text{constant.}$$

If w is the energy consumed per second in the dissociation process, then w must be equal to nQ where Q is the heat of dissociation, and

$$\log_e \frac{w}{Q} = -\frac{E}{RT} + \text{constant}.$$

Since Q is a constant, the value of E can be determined from the slope of the 1/T — log w curve. The value of E obtained was 35,700 calories per gram-molecule, a value which is almost the same as the heat of dissociation of gaseous iodine determined by the direct methods (36,800 cals./gm. mol., Birge and Sponer, 'Phys. Rev.,' vol. 28, p. 259 (1926)). But it is only approximate and it is unlikely that the heats of dissociation of iodine in the gas phase and on the platinum surface are the same. The agreement, however, is sufficient to support the hypothesis that the process occurring is in fact the dissociation of the molecular iodine into atoms.

When the actual rate of dissociation is calculated, a discrepancy between the two methods appear. By identifying the rate of fall of pressure in the former experiments with the rate of formation of atoms at the surface of the wire, $3 \cdot 6 \times 10^{-11}$ gram-molecules per second at 1297° K. is obtained. In the experiments on energy losses from the wire, the rate of dissociation should be given by $n = w/Q$ gram-molecules per second. At 1290° K. $n = 5 \times 10^{-8}$, a value one thousand times as great as that obtained by the other method. It is interesting to note that Langmuir observed a similar discrepancy in his experiments on the dissociation of hydrogen.*

After about 12 " clean-up " experiments, the rates of fall of pressure began to diminish, and after about the fifteenth run, there was no decrease in pressure at all, in spite of repeated heating of the walls of the vessel. A rough computation of the amount of platinum evaporated on to the glass walls during the previous runs and outgassing of the filament, was made, utilising Langmuir's figures for the rate of evaporation of platinum at different temperatures.† It was found that the minimum amount of platinum deposited on the glass must have been $1 \cdot 1 \times 10^{-4}$ gram. The available area of the walls was 70 sq. cm., which gives an area per atom of about $2 \cdot 0$ A°^{2}. The area of a platinum atom is about 12 A°^{2} so the walls were covered, at this stage, with a platinum layer only a few atoms thick. Evidently, then, this layer can catalytically accelerate the recombination of adsorbed iodine atoms, just as thick metallic films accelerate the rate of recombination of the atoms of hydrogen.* The pressure, therefore, does not fall as before, but remains constant, as the atoms formed at the hot filament undergo recombination on this layer and return to the gas phase as molecules.

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* 'J. Amer. Chem. Soc.,' vol. 37, p. 451 (1915).

† 'Phys. Rev.,' vol. 4, p. 377 (1914).

(*b*) *The Surface Attack of Platinum by Iodine Atoms.*

The action of the platinum film in eliminating the fall in pressure due to the adsorption of the iodine atoms on the glass, was very fortunate, as it was then possible to proceed to higher temperatures, and to study the kinetics of the attack of the platinum by the iodine by observations of pressure changes.

The rates of attack were obtained from the experimental curves of the pressure of the iodine vapour plotted against the time, over a range of filament temperature of from 1440° K. to 1560° K. The reaction vessel was heated to 200° C. between each run to decompose the iodide formed and to leave a surface of fresh platinum.

It was found that the rates of attack at the lower temperatures obeyed the relation $-dp/dt = a + bp$ or $\log (a + bp) = - ct +$ constant. Fig. 1 shows some of the experimental pressure-time curves, from the slopes of which, values of a and b, given in the table, were obtained. Fig. 2 shows the relationship between $\log (a + bp)$ and t.

Experiment.	Temperature (° K.).	$b \times 10^4$.	$a \times 10^4$.
55	1441	2·23	0·007
47	1442	2·37	0·007
51	1452	2·60	0·009
49	1485	4·17	0·043
48	1489	4·23	0·044
50	1513	6·60	0·085
46	1526	6·93	0·087
44	1538	8·13	0·127
43	1558	9·50	0·167

The curves show, however, that at the higher temperatures, the rates begin to fall off from the relation $dp/dt = a + bp$ at the lower pressures, the divergence beginning at higher pressures, the higher the temperature. The following table gives the values of the critical pressures :—

Experiment.	Temperature (° K.).	p_c.
51	1452	0·0020
49	1485	0·0030
46	1526	0·0049
44	1538	0·0057

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* Bonhoeffer, 'Z. Phys. Chem.,' vol. 113, p. 199 (1924); Taylor, 'J. Amer. Chem. Soc.,' vol. 52, p. 1910 (1930).

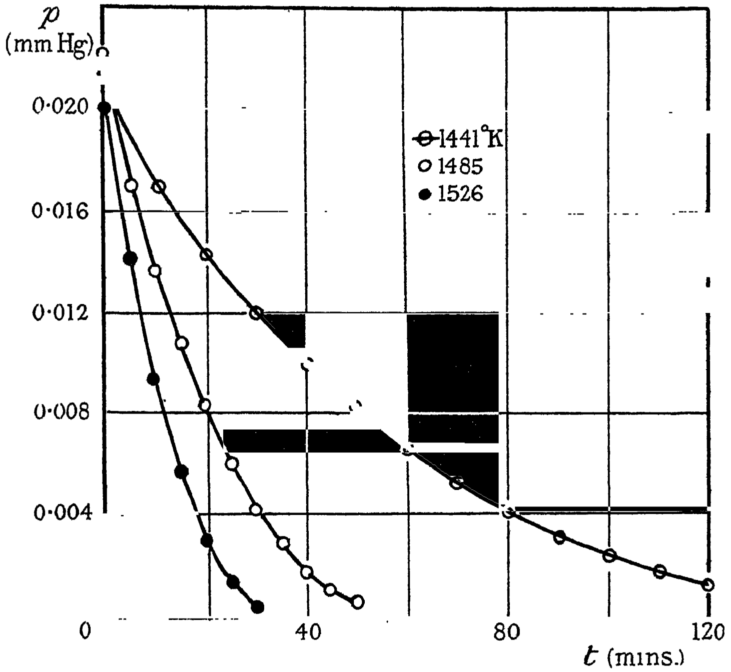
p (mm Hg)
0·020
0·016
0·012
0·008
0·004
0
40
80
120
t (mins.)
1441°K
1485
1526

FIG. 1.

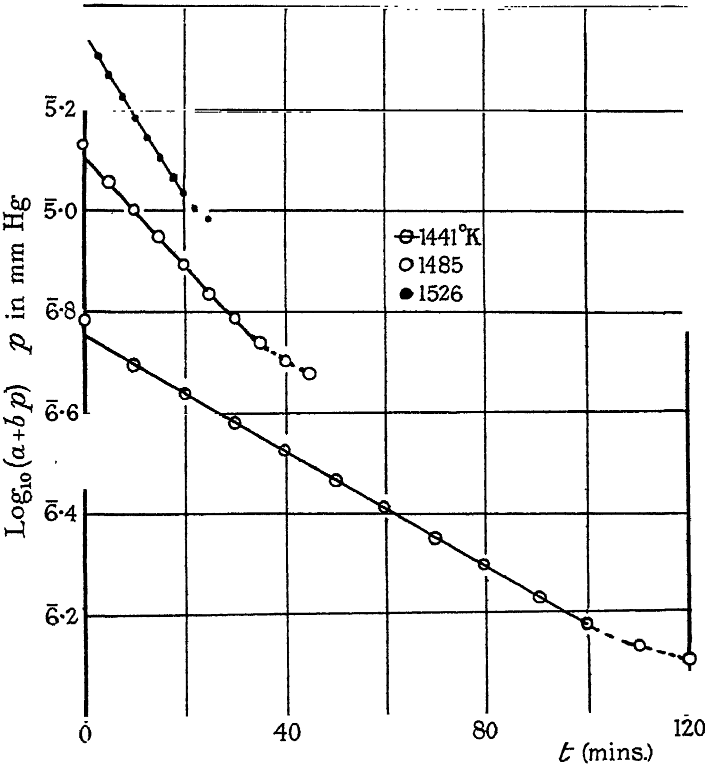
$\text{Log}_{10}(a+bp)$ p in mm Hg
$\bar{5}$·2
$\bar{5}$·0
$\bar{6}$·8
$\bar{6}$·6
$\bar{6}$·4
$\bar{6}$·2
0
40
80
120
t (mins.)
1441°K
1485
1526

FIG. 2.

Interpretation of the Kinetics.

The zero-order term " a " is due to the clean-up of iodine as Pt I which forms a unimolecular layer on the surface of the platinum and evaporates at a rate independent of the pressure. The component " bp " is due to the formation of Pt I_2 by the attack of the Pt I adsorption complex by iodine atoms, at a rate proportional to the iodine pressure. Below a certain critical pressure the surface of the metal is bare, and the formation of Pt I also becomes a first-order process. Since the rate of formation of Pt I_2 rapidly becomes negligible compared with that of Pt I, the reaction should become unimolecular, and this is in fact the case.

The experiments of Kalandyk on the thermionic emission of platinum support this interpretation. He found that the presence of 0·03 mm. of iodine vapour enhanced the emission at 1220° K., slightly increased it at 1440°, but was without effect at 1600°, *i.e.*, a platinum surface at 1600° K. in iodine at 0·03 mm. is bare. The effect of increasing the iodine pressure was to increase the emission roughly proportionally; no values are given for pressures lower than 0·03 mm., but by extrapolation of our results, it is found that the critical pressure becomes 0·03 mm. at a temperature of 1605° K., which supports the view that the critical pressure does indeed mark the point at which the surface is no longer covered by an adsorbed layer of Pt I.

In fig. 3 is given a plot of log a against 1/T, which is approximately linear and gives a value for the " apparent " energy of activation for the formation of Pt I of 96,000 calories per gram-molecule. The corresponding value for the

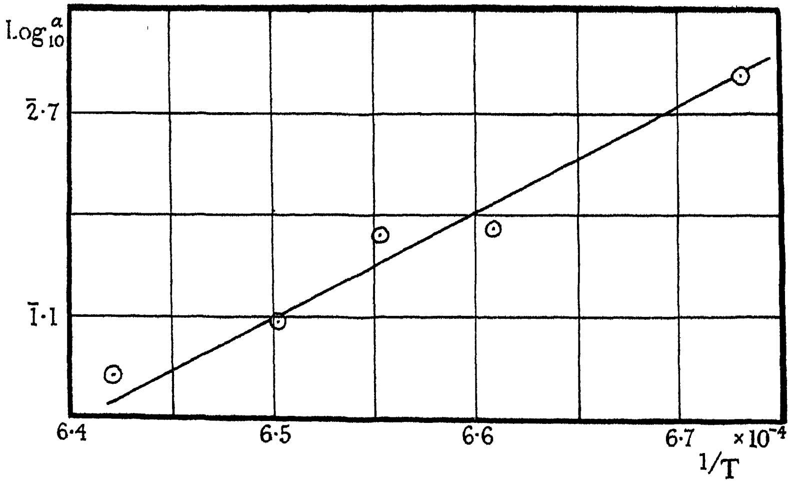

FIG. 3.

$Pt\,I_2$, obtained from a plot of log *b* against 1/T, shown in fig. 4, is 57,800 calories. The energy of vaporisation of metallic platinum is 124,000 calories,

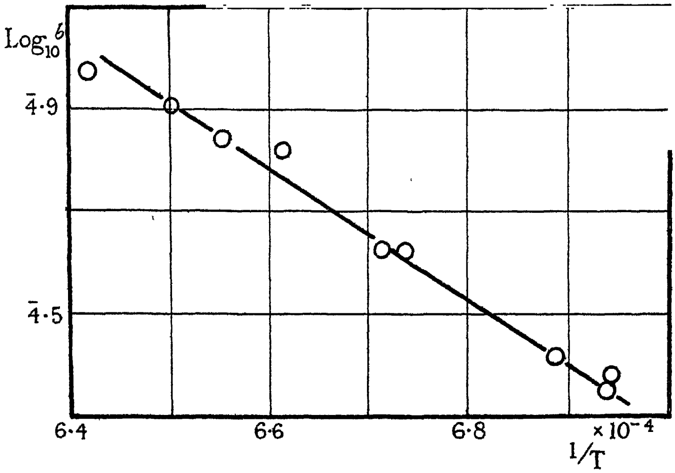

FIG. 4.

and it is interesting to note that the rupture of the Pt-Pt bond is progressively facilitated by the addition of the iodine atoms to the evaporating platinum atom.

— Pt–Pt	124,000 calories per gram-molecule.		
— Pt–Pt I·	96,000	,,	,,
— Pt–Pt I_2	57,800	,,	,,

Summary of Experimental Part.

The attack of platinum by iodine is a two-stage process. At relatively low temperatures no surface attack occurs, but at about 1300° K. dissociation of the molecular iodine takes place. About 1400° K. the atomic iodine attacks the metal forming the volatile iodides Pt I and $Pt\,I_2$.

Absolute Rates of the Reactions.

That neither the dissociation of molecular iodine nor the formation of $Pt\,I_2$ is simply the result of suitable high speed collisions between the iodine and the surface is evident from the following table, where the rates given in the last column are calculated from the expression $n_0e^{-E/RT}$, which is the fraction of the total number n_0 of molecules colliding with the surface which acquire energy greater than E, the apparent energy of activation obtained from the Arrhenius equation.

	Experiment.	Temperature (° K.).	Observed rate in molecules per second at 0·01 mm. Hg.	Calculated rate.
Dissociation E = 41,700	22 25	1297 1345	$0{\cdot}73 \times 10^{13}$ $1{\cdot}3 \times 10^{13}$	$4{\cdot}3 \times 10^{10}$ $6{\cdot}5 \times 10^{10}$
Attack E = 57,800	51 44	1452 1538	$2{\cdot}2 \times 10^{11}$ $6{\cdot}9 \times 10^{11}$	$1{\cdot}8 \times 10^{7}$ $5{\cdot}3 \times 10^{7}$

The reactions cannot, therefore, be the result of a simple "collision" process, but must occur subsequent to adsorption of the gas on the surface, and involve some other mechanism of activation.

The distribution of molecules between the free space and the adsorbed layer as a first approximation may be assumed to follow the distribution law of Boltzmann and expressible by the relationship $n_0 = ne^{\lambda/\mathrm{RT}}$, where n_0 is the concentration per cubic centimetre in the adsorbed layer, n that in the gas phase and λ the difference in potential energy involved in the transfer of a gram-molecule from one phase to the other. If the area of the platinum surface be A and the thickness of the adsorbed layer be δ, the number of molecules adsorbed will be $\mathrm{A}\delta n e^{\lambda/\mathrm{RT}}$. Of these a fraction $e^{-\mathrm{E}/\mathrm{RT}}$ will possess sufficient energy to undergo reaction and if ν be the specific rate of reaction, the rate will be given by

$$\mathrm{A}\delta n \nu e^{-\frac{(\mathrm{E}-\lambda)}{\mathrm{RT}}},$$

where $(\mathrm{E} - \lambda)$ is the "apparent" energy of activation.* In this equation we may equate δ to the diameter of an iodine molecule on the assumption of the existence of a unimolecular layer. A, n and $(\mathrm{E} - \lambda)$ are directly measurable quantities. Some uncertainty exists as to the evaluation of ν, but in processes of evaporation† and sublimation, as well as in certain heterogeneous decompositions,‡ it has been identified with the atomic vibration frequency of the substrate. The results of the application of this expression for the rate of reaction are shown below.

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* *Cf.* Hinshelwood and Topley, 'J. Chem. Soc.,' vol. 123, p. 184 (1923).

† S. Dushman, 'J. Amer. Chem. Soc.,' vol. 43, p. 397 (1921); E. K. Rideal, 'Proc. Camb. Phil. Soc.,' vol. 20, p. 291 (1921).

‡ Polanyi and Wigner, 'Z. Phys. Chem.,' vol. 139, p. 439 (1928); B. Topley, 'Nature,' vol. 128, p. 115 (1931).

The Dissociation Process.

Data.

Measured area of filament A	0·352 cm.^{2}.
Diameter of iodine molecule	3·76 A°.
Concentration n at pressure 0·01 mm. Hg	3·56 × 10^{14} mols. per c.c.
ν for platinum	4·36 × 10^{12} sec.$^{-1}$.
Measured $(E - \lambda)$	41,700 calories.

Experiment.	Temperature (° K.).	dp/dt at p=0·01 mm. Hg per sec. in 120 c.c.	Rate in molecules per sec.	Rate of activation mols. per sec.	Ratio F.
22	1297	1·7 × 10^{-6}	0·73 × 10^{13}	0·18 × 10^{13}	4·0
25	1345	3·0 × 10^{-6}	1·3 × 10^{13}	0·30 × 10^{13}	4·3

The theory therefore gives the right order of magnitude for the rate of dissociation. The rates differ from the experimental values by a factor of four, which may well be due to an "area factor." This is confirmed in the case of the formation of PtI_2.

Formation of PtI_2.

Data.

Diameter of iodine atom	2·6° A.
Concentration at 0·01 mm. Hg	7·1 × 10^{14} atoms per c.c.
Measured $(E - \lambda)$	57,800 calories.

Experiment.	Temperature ° K.).	Rate in atoms per sec. at p = 0·01 mm. Hg.	Rate of activation in atoms per sec.	Ratio.
51	1452	2·2 × 10^{11}	0·52 × 10^{11}	4·3
48	1489	3·6 × 10^{11}	0·86 × 10^{11}	4·2
44	1538	6·9 × 10^{11}	1·6 × 10^{11}	4·4

The third column is calculated from the experimental values of the rates of surface attack (as given by the coefficient "b") at a pressure of 0·01 mm. Hg. Again the theory gives results of the same order of magnitude as experiment, differing again by a factor of four, which is not an unreasonable value for the area factor.

The Heat of Adsorption of Atomic Iodine on Platinum.

At the "critical pressures," when the surface is just covered with the Pt I complex, the number of iodine atoms present in the adsorbed layer should be the same over the temperature range examined. Assuming that the Boltzmann law gives the density in the adsorbed layer, the number of atoms adsorbed is $kp\,e^{\lambda/\mathrm{RT}}$ and therefore $kp_c\,e^{\lambda/\mathrm{RT}}$ = a constant, or $\log_e p_c = -\lambda/\mathrm{RT} +$ a constant. Fig. 5 shows a plot of $\log p_c$ against 1/T, which is linear, and from which a value of 53,700 calories per gram-molecule is obtained for the heat of adsorption of the atomic iodine on platinum.

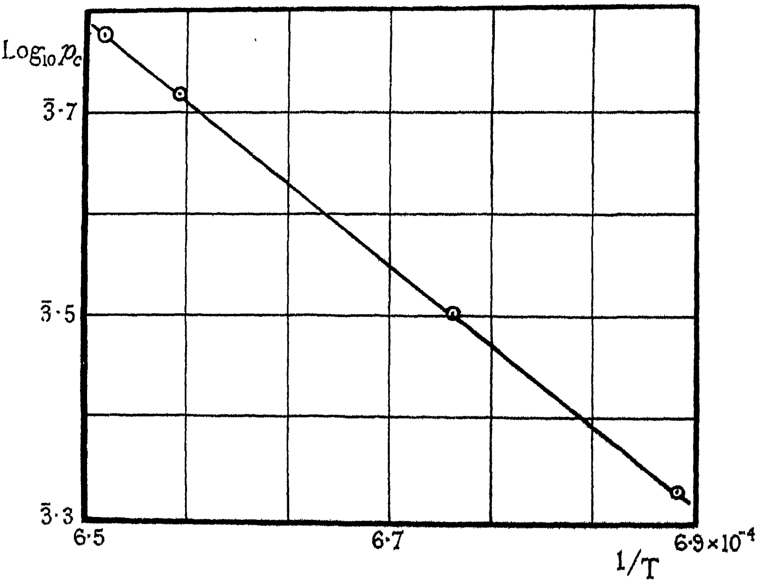

FIG. 5.

The number of iodine atoms adsorbed on the filament at the critical pressure is given by the expression $\mathrm{A}\delta n_c e^{\lambda/\mathrm{RT}}$, and on insertion of the experimental values we obtain $1\cdot7 \,.\, 10^{13}$ atoms. For a closely packed unimolecular layer of atoms the number would be A/σ or $6\cdot6 \,.\, 10^{14}$ atoms, thus at the critical pressure the packing is such that the " effective area " of an iodine atom is some forty times the actual area, a value which lends some support to the hypothesis that the layer, at these temperatures at least, is mobile.

The Attack of Tungsten by Iodine.

The apparatus and experimental method were similar to those used in the experiments on platinum. The tungsten filament, 0·005 cm. in diameter and 11·8 cm. long, was welded to platinum leads and a small hoop of thick tungsten wire was hung on the filament to prevent it from touching the sides of the vessel. The vessel was baked out at about 300° C. for several hours, and the filament " outgassed " by heating *in vacuo* to about 1500° C. for 2 hours. The temperature of the wire was found from measurements of the resistance by means of the expression

$$R_t = R_0 (1 + 0{\cdot}00538t + 0{\cdot}0000007t^2).$$

Low Temperature Observations.—Unlike platinum, tungsten is attacked by iodine at low temperatures, forming a non-volatile iodide. The rate of clean-up was found to be inversely proportional to the amount of iodine removed, *i.e.* to the thickness of the iodide film formed. The process controlling the rate of reaction is therefore the diffusion of iodine through the iodide film. Measurements were made at temperatures of from 273° K. to 1300° K. The results of a specimen run are shown in the Table. The film could be removed by glowing the wire at about 1300° K. *in vacuo,* when the tungsten iodide did not evaporate but was dissociated.

Experiment 7. $T = 810°$ K. $(p_0 - p)^2 = kt$.

t (minutes).	p.	$(p_0 - p)^2 \times 10^6$.	k.
0	0·0254	0	—
5	0·0232	4·8	0·96
10	0·0224	9·0	0·90
15	0·0211	18·5	1·23
20	0·0207	22·1	1·10
25	0·0203	26·0	1·04
30	0·0200	29·2	0·97
35	0·0193	37·2	1·06
40	0·0189	42·4	1·06

At the temperature usually employed, viz., 2100° K., the film decomposed into iodine atoms. These were adsorbed on the glass, and when the walls of the vessel were heated, the pressure increased by an amount almost equal to the decrease during the formation of the film. However, if the filament was glowed at a lower temperature, viz., 1460° K., the film decomposed partly into molecules as indicated by the rise in pressure, and partly into atoms. The following table summarises one of the experiments, in which a thick film was decomposed alternately at 1460° and 2100° K.

Filament glowed out—		Pressure of iodine formed as—	
At Temperature° K.	For t minutes.	(1) Molecules.	(2) Atoms.
1460	20	0·0043	0·0069
2100	2	0	0·0040
1460	10	0·0030	0·0045
2100	10	0	0·0019
1460	10	0·0005	0·0016
		Total = 0·0267	

The pressure corresponding to the amount of iodine used to form the film was 0·0284.

The rates of formation of the iodide film were very small, and a more sensitive means of detecting its presence than the fall in iodine pressure was desirable. Measurements were made of the emissivity of the bare wire and of the wire coated with iodide, and it was found that when the same standard current was passed through them, the covered wire reached a higher temperature than did the bare wire. The procedure adopted will now be described.

The filament was glowed out at 2100° K. in a good vacuum and allowed to cool. A " standard " current was then passed through until a steady temperature was reached, as indicated by the resistance measurements. A charge of iodine at 0·027 mm. was then admitted and pumped off after a period of 5 minutes. The wire was again heated with the standard current and the temperature reached measured. This temperature was considerably higher than before, showing that a film of iodide had been formed on the surface of the wire. A further measurement of the emissivity, after glowing the wire *in vacuo*, showed when the wire was bare again. The results of a typical experiment are shown below.

Treatment of filament.	Temperature of filament when heated *in vacuo* with 0·04 amps.	Inference.
	° C.	
Glowed *in vacuo* at 2100° K. for 10 minutes	44	—
Heated in iodine vapour at 0·027 mm. Hg at 44° C. for 5 minutes	80	Film formed.
Glowed *in vacuo* at 1420° K. for 3 minutes	60	Film partly removed.
Glowed *in vacuo* at 2100° K. for 2 minutes	45	Surface bare again.

Experiments were then made to determine whether a definite dissociation temperature existed for the iodide in the presence of 0·027 mm. of iodine vapour. The filament was heated at various temperatures in iodine at 0·027 mm., and the formation or non-formation of a film of iodide determined by the emissivity method. The Table (p. 401) summarises the results.

This shows that below 1445° K. the compound is formed and above 1505° K. it is not. It was not possible to narrow down this range any further, owing to the practical difficulty of removing the iodine while the wire was still at T° K. without decomposing the film which might have been formed. Care was taken that the heating current was not switched off until all the iodine had been removed (by connecting directly to a vessel cooled in liquid air) as

Experiment.	Standard current in amperes.	Temperature of filament when heated *in vacuo* by standard current ° K.		Temperature T° K.	Film formed.
		Before heating at T° K. in iodine.	After heating at T° K. in iodine.		
1	0·045	495	507	375	Yes
3	0·045	493	501	970	Yes
5	0·030	311	354	1280	Yes
6	0·030	313	340	1440	Yes
7	0·030	313	321	1445	Yes
2	0·045	495	495	1505	No
8	0·030	316	316	1530	No

indicated by the Pirani gauge, so that the positive evidence for the formation of a film at 1445° K. is reliable, and not due to film formation on the cooling wire by residual iodine.

The narrowness of the temperature range strongly suggests that the film is behaving as a compound with a definite dissociation pressure, rather than as an adsorption complex. A rough computation indicates that the film is some 10 molecules in thickness. Unfortunately, by this method it was impossible to find out whether there is an extension of the temperature range for thinner films.

The Dissociation of Iodine into Atoms.

When the filament was heated in iodine to temperatures below about 1400° K., no formation of atomic iodine could be detected. In an experiment in which the filament temperature was 1300° K. the pressure fell in accordance with the diffusion law, and became steady at 0·018 mm. Hg. This was due to the formation of a film of iodide on the wire, and not to the dissociation of the iodine into atoms and their subsequent adsorption of the glass, since on heating the walls of the vessel after the " clean-up " had finished, there was no rise in pressure. But when the filament temperature was raised to 1420° K. the pressure fell below 0·018 mm. at a very slow rate, and when the walls of the vessel were heated and the ice-bath replaced, the pressure had risen, showing that atomic iodine adsorbed on the glass had come off again as molecules.

The temperature was then raised to 1860° K., when a fall in pressure occurred, which was due entirely to the removal by the glass of iodine atoms formed at the hot filament. This was proved by the fact that the iodine which had disappeared was always completely recovered when the walls of the vessel were heated. The rate of fall in pressure was proportional to the iodine pressure.

Measurements were then made at higher temperatures, and it was found that the process had a very small temperature coefficient. The details of two experiments are given in the tables.

Experiment 26. T = 1960° K.

t (minutes).	p (mm. Hg).	$\text{Log}_{10}\, p$.
5	0·0230	$\bar{2}$·362
15	0·0193	·285
25	0·0176	·245
35	0·0164	·214
45	0·0146	·164
55	0·0131	·117
65	0·0121	·083
75	0·0112	·050
85	0·0104	·017

Experiment 28. T = 2100° K.

t (minutes).	p (mm. Hg).	$\text{Log}_{10}\, p$.
0	0·0254	$\bar{2}$·405
10	0·0225	·352
20	0·0199	·299
30	0·0169	·228
40	0·0148	·170
50	0·0130	·114
60	0·0115	·061

The rates of dissociation varied to some small extent with the condition of the wire, but were quite reproducible if the surface was sintered before each experiment by glowing the filament at 2100° K. for half an hour.

(c) *The Attack of Tungsten by Iodine Atoms.*

The atomic iodine formed at the filament did not attack the hot metal as there was no measurable change in its resistance. But the cooled parts of the filament were attacked, and a brown deposit appeared on regions of the glass vessel opposite the join of the filament to the leads and the point of suspension of the thick tungsten hoop. The iodide formed must therefore have been volatile at some intermediate temperature, and was evidently a different compound from that formed in the attack of the tungsten by molecular iodine.

Langmuir found that a hot tungsten filament was also unaffected by chlorine, but a cold filament placed nearby in the reaction vessel was attacked by the chlorine atoms formed at the hot wire.*

Calculation of Absolute Rate of Dissociation.—Dissociation of iodine on tungsten occurs at a very much slower rate than on platinum. This can be ascribed to the difference in the adsorptive powers of the two metals for iodine. Experiments by Kalandyk on the thermionic emission of platinum and tungsten in iodine vapour show that the gas is adsorbed on the platinum but not on the tungsten over the temperature ranges used. So it is not surprising that the mechanism which was found to account quantitatively for the rates of dissociation on platinum, and which assumes that the gas is first adsorbed and then derives energy from the vibrating atoms of the solid, in the case of tungsten, gives rates which are considerably greater than those found experimentally. The observed rates are quite well represented, however, by the simple "collision" mechanism, where the number of molecules dissociated per second is given by $n_0 e^{-E/RT}$, where n_0 is the total number of molecules striking the wire, and E is the ordinary heat of dissociation of molecular iodine. The observed rates of dissociation and those calculated from this expression are given in the following table.

Experiment.	Temperature T° K.	dp/dt at 0·01 mm. Hg in 110 c.c.	Observed rate in molecules per second.	Calculated rate.	Ratio.
24, 26, 30	1860	$1{\cdot}49 \times 10^{-6}$	$5{\cdot}25 \times 10^{12}$	$11{\cdot}1 \times 10^{12}$	0·47
28, 29 30	2100	$2{\cdot}30 \times 10^{-6}$	$8{\cdot}11 \times 10^{12}$	$35{\cdot}1 \times 10^{12}$	0·23

Comparison of Tungsten with Platinum.—Although iodine attacks tungsten at low temperatures forming a non-volatile iodide, no such compound could be detected in the case of platinum from temperatures from 278° K. to 1700° K. The emissivity of the platinum was unaltered by the action of iodine over this temperature range. So this method, although capable of detecting the film of compound some 10 molecules thick formed on the tungsten, cannot detect the unimolecular adsorbed layer of the complex Pt I which is formed on the surface of the platinum at all temperatures below about 1560° K. Langmuir noted that the adsorption complex W — O was similarly without effect on the characteristics of the tungsten filament.†

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* 'J. Amer. Chem. Soc.,' vol. 37, p. 1162 (1915).

† 'J. Amer. Chem. Soc.,' vol. 38, p. 2271 (1916).

Dissociation of molecular iodine takes place much more readily on platinum than on tungsten, owing to the stronger adsorption of the gas on the former metal, which in turn may be ascribed to its higher work function.

Atomic iodine does not attack the hot tungsten on which it is formed, but combines with the cool metal in the neighbourhood, so the compound formed is evidently unstable at the high temperatures. In the case of platinum, the compound formed, *i.e.*, Pt I, is probably endothemic, because $PtCl_4$ and PtCl have heats of formation of respectively 262 and 70 kilojoules per gram-molecule, whereas PtI_4 is exothemic to the extent of only 70 kilojoules. The Pt I would, therefore, be stable at high temperatures, and attack of platinum by atomic iodine could occur there, though not occurring in the cold.

On the Contact of Smooth Surfaces.

By S. H. Bastow and F. P. Bowden, Laboratory of Physical Chemistry, Cambridge.

(Communicated by Sir William Hardy, F.R.S.—Received July 7, 1931.)

In recent years a number of experiments have shown that if a clean optically polished plate is lowered on to a similarly polished plate in air, the two surfaces do not come into contact. The top plate remains "floating" at a distance equal to the thickness of several thousand air molecules above the bottom plate. Thus Hardy and Nottage* found that a polished steel cylinder placed on a steel plate remained at a distance of 4 μ above the plate in clean dry air. By applying a pressure to the top cylinder the surfaces could be made to approach more closely, but on removing the pressure the cylinder would again rise to a height of 4 μ. This height remained constant and was the same for glass on glass as for steel on steel.

When the air was replaced by various organic substances, *e.g.*, octane, caprylic acid, octyl alcohol, the distance between the surfaces remained remarkably constant at 4 μ. When the surfaces were contaminated with a trace of palmitic acid the distance was decreased to 2·3 μ. Similarly Watson and Menon† using an electrical capacity method found that the distance between polished silver or polished steel plates in air or in oil was approximately 4 μ. Experiments made by Lee* are consistent with this. A full discussion of this phenomena is given by Hardy,† who considers it to be "the most difficult problem of the boundary state" (*loc. cit.*, p. 2). The possibility that the top plate is supported on solid particles was considered in this paper, but the experimental evidence then available argued against it, and it was thought probable that the plate was supported by a film of air or of liquid. To explain this it would be necessary to postulate oriented chains of molecules extending from the surface for several thousand molecules. This is contrary to most physical evidence, which shows that the effect of a surface on a gas does not extend for more than a few molecular layers. The first molecular layer of gas may be oriented and strongly held by the surface, but the degree of orientation decreases very rapidly and becomes inappreciable at a distance of a few molecular diameters from the surface. The point was discussed with Sir William Hardy, and at his suggestion further experimental work was undertaken on this anomalous effect.

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* 'Proc. Roy. Soc.,' A, vol. 118, p. 209 (1928).

† 'Proc. Roy. Soc.,' A, vol. 123, p. 185 (1929).

The work shows that it is very difficult to place surfaces together without dust or solid particles coming between them. When somewhat elaborate precautions were taken and the surfaces were scrupulously clean there was no evidence for "floating." A polished glass plate lowered on to a similar plate in air at atmospheric pressure sank down quickly to within 0·45 μ of it. This small distance was the same whether the plates were in high vacua, alcohol vapour or nitro-ethane vapour and it was not affected by changes of gas-pressure. Similar experiments in pure liquid alcohol or water gave the same result: the top plate sank slowly down to within 0·3 μ. Each plate was smooth to approximately 0·25 μ and this small remaining separation is almost undoubtedly due to the surface irregularities in the glass or to very small dust particles which have not been excluded.

Preliminary Experiments.

The two glass plates used were supplied by Messrs. Adam Hilger. The larger of these was 3 cm. square and the smaller 2 cm., and each was about 3 mm. thick. Their surfaces were plane to one Newton ring and parallel to one minute. The edges were bevelled, so that the plates could be gripped by tweezers without touching or damaging the polished surfaces.

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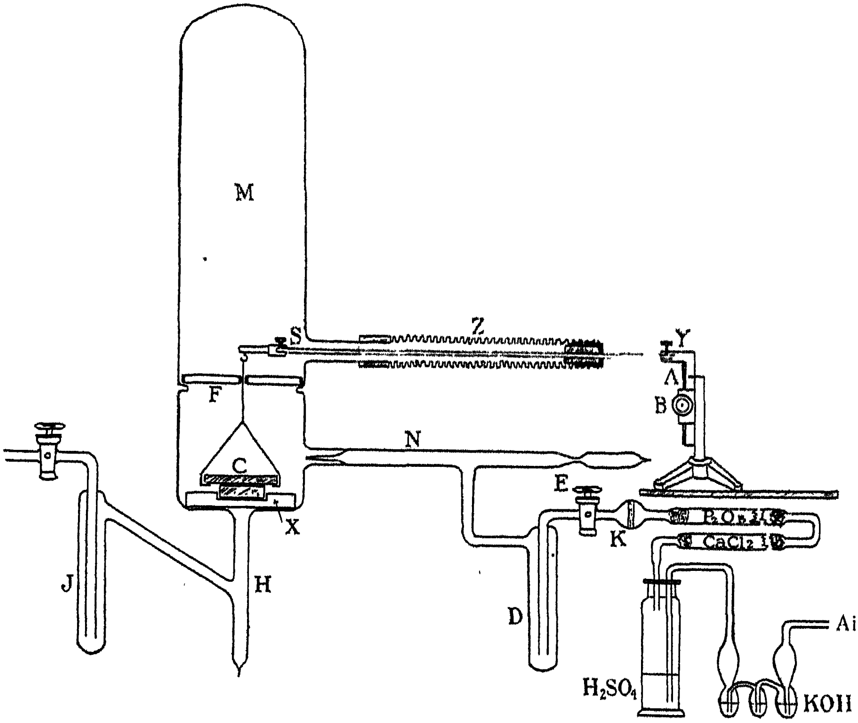
* "Science Progress," October, 1930, p. 219.

† 'Phil. Trans.,' A, vol. 230, p. 1 (1931).

On cleaning these surfaces and placing them gently together in the air of the laboratory they did not usually come into close contact. When viewed in white light coloured fringes were not visible; but when viewed in monochromatic light numerous interference bands of high order could be seen, showing that the plates were separated by a distance of several μ. On careful examination it was sometimes possible to see small dust particles between the plates. Precautions were then taken to eliminate dust.

Apparatus.

A diagram of the apparatus is shown in the accompanying figure. A large glass cylinder (M), which was originally open at one end, was connected by a small tube sealed into the other end to a high vacuum pump and a McLeod gauge.



The smaller polished plate rested loosely in a depression 1 mm. deep, etched out of the glass block (X), which rested on the bottom of the cylinder. The larger polished plate was carried by a light brass framework suspended by fine platinum wire. The platinum wire was attached by a hook and a small brass collar to the end of the steel rod (S). The other end (Y) of the steel rod was carried by a solid copper plug fitting into the end of the flexible corrugated copper tubing (Z). One end of the flexible tubing was connected to the glass cylinder by a copper to glass seal, and the other end attached to the rack and pinion (A). Turning the screw head (B) gave a vertical motion to the rod (S) which lowered or raised the top polished plate (C). This movement was very sensitive and easily controlled. A small steel bar was fitted into the brass framework which carried the polished plate and by bringing a magnet near the apparatus the plate could be moved in a horizontal plane or rotated.

Air or vapour could be admitted to the cylinder by the side tube (N). The air was bubbled through caustic potash solution and strong sulphuric acid and then passed over calcium chloride and long tubes containing P_2O_5. It was filtered by passing through glass wool and finally through the very small capillaries in a plug of sintered glass (K). This had previously been thoroughly cleaned in nitric acid and conductivity water and baked dry in an air oven for 3 hours at 200° C. The air was admitted through the tap (E) which was eventually greased with Apiezon grease and protected from the rest of the apparatus by the liquid air trap (D). The glass disc (F) served to protect the plates from dust during the sealing off of the cylinder. The platinum suspension wire passed through a small hole drilled in the centre of this disc. When the apparatus was assembled and the end of the cylinder sealed off, the cylinder could be evacuated through the tube (H). The liquid air trap (J) prevented any grease from reaching the cylinder from the taps in the high vacuum line.

Cleaning and Illumination of Plates.

The two optically smooth plates were washed in dilute nitric acid and the surfaces sponged with a swab of cotton wool which had been softened to a pulp by immersion in strong nitric acid. They were then thoroughly washed in quick succession with conductivity water and ethyl alcohol and finally immersed in a large closed bath of carefully purified ethyl alcohol. This alcohol had been twice re-distilled in an all-glass still and was stored in a flask from which it could be siphoned without exposure to the air. This was done to minimise contamination by dust particles, but it is difficult to obtain a liquid quite free from dust. Under the ultra-microscope this alcohol showed occasional small dust particles.

When the plates were finally in position they were illuminated by an 800 candle-power lantern lamp, placed behind a ground-glass screen. The light was incident at an angle of 45°.

When interference fringes were formed they were examined by focussing the plates on to the ground glass plate of a large reflex camera, fixed in position with its axis on the beam of light reflected from the plates. This, a convenient method of ensuring a constant angle of vision, is necessary since the position of the fringes depends on the angle from which they are observed.

Monochromatic illumination was provided by a sodium burner.

Assembly of Apparatus.

The glass cylinder, while still open at the top, was thoroughly washed with pure alcohol and closed with a porcelain lid. The ground glass block (X) and the brass frame for the larger optically smooth plate were both cleaned in nitric acid, conductivity water, and alcohol. They were then immersed with the two polished plates in the large bath of pure alcohol. The three plates were then lifted by a long pair of pliers and quickly placed on the bottom of the glass cylinder. The two polished plates were still covered by a pool of alcohol. The glass protecting plate was placed above them and the platinum suspension of the carrier was threaded through it and hooked on to the movable steel rod (S). The top of the cylinder was then sealed off, care being taken that the flame of the blowpipe used did not play on the open mouth.

The plates, which could be moved about at will, were now enclosed in a vessel, free from tap grease, which could be evacuated or filled with clean air.

Experimental.

The vessel was now pumped out and the alcohol evaporated off. During the final stages of the pumping the top plate was lifted away from the bottom plate to ensure that no alcohol vapour could be imprisoned between the surfaces. The pressure was reduced to 10^{-5} mm. and on shutting off the pump it remained constant at this value, showing that there was no leak nor was alcohol vapour present. The vessel was then allowed to fill with clean dry air; during the filling the surfaces were placed very close together so that any possible dust coming in with the air could not get between them. When the vessel was full of air at atmospheric pressure, the top plate was lifted clear of the bottom plate.

The micrometer screw (B) was then slowly turned and the interference fringes observed as the top plate was allowed to sink under its own weight on to the bottom plate. The weight of the top plate was 6 grams and the area of the bottom plate 4 sq. cm. so that the pressure on it was only 1·5 gm./cm.^{2}. At first the surfaces were too far apart for any interference bands to be seen, but as they came closer very fine fringes were visible when the plates were illuminated with sodium light.

The top plate was seen to be slightly tilted and at a distance of about 10 μ above the lower plate. As the lowering was continued the fringes broadened and decreased in number, and finally coloured fringes appeared when white light was used. Coloured fringes are not visible in air films thicker than 2 μ (see Lawrence, "Soap Films," p. 137) so the plates were already closer than this.

The colour fringes of a lower and lower order passed regularly across the plate until finally the plate came to rest under its own weight. The characteristic colour of the second order violet was visible on one corner, indicating a separation of ca. 0·28 μ; the opposite corners were ca. 0·61 μ apart. The plates were now separated only by a mean distance of 0·45 μ. They had not seized, and the experiment could be repeated indefinitely, the plate always sinking to the same level. The time required for it to fall to the equilibrium position was approximately three seconds. Gently tapping the apparatus when the plates were lowered caused no shift in the bands.

Effect of Varying Gas Pressure.

The top plate was raised and the cylinder evacuated to 10^{-5} mm. After about 10 minutes the plate was re-lowered. The interference bands passed through the same stages and *the final equilibrium position was identical with that observed in air.* The only difference observed was that the plate fell rapidly to this position instead of taking 3 seconds. The slow descent at atmospheric pressure is to be expected, since the air must take time to escape from the narrow space between the plates.

On admitting air to the evacuated vessel so that the pressure rose rapidly to atmospheric, the bands did not shift. There was no rise of the top plate. These experiments were repeated several times *in vacuo*, in air at 0·3 mm. pressure, and in air at 10 cm. pressure. The plate always sank to the equilibrium distance and this distance was not increased when the pressure rose.

If the air was admitted very suddenly a slight broadening of the fringes was observed for an instant. Apparently the air took some time to diffuse into the narrow space between the plates; the pressure on the top plate was, momentarily, increased and the plates forced more closely together. This effect was slight, probably less than 0·05 μ.

A very violent blast of air blowing on the plate could lift it mechanically, but it dropped back again to the equilibrium position.

When the surfaces are placed gently in contact in this way they do not "seize" even *in vacuo*; a very small force is sufficient to separate them again. At the end of the experiment, when the cylinder was opened, a pressure of several pounds was applied to the top plate. There was only a very small decrease in the distance between the plates, the mean distance decreased from 0·45 μ to 0·38 μ and it was not possible to force them more closely together. The plates now adhered to one another and it required some force to separate them.

Experiments in Vapour.

If it is possible for oriented chains of polarised molecules to extend to large distances from a surface one might expect to find them more readily in a highly polar substance such as alcohol or water. Experiments were therefore made in alcohol vapour, nitro-ethane vapour and water vapour.

A small glass bulb, half-full of alcohol, was sealed on to the air line. The apparatus was then evacuated and the alcohol allowed to evaporate till readings on the McLeod gauge indicated that the pressure in the cylinder was that of alcohol at room temperature.

The top plate was then raised well above the other, and after about 10 minutes it was lowered. Again it took up the equilibrium position distant about 0·4 μ above the bottom plate. Subsequent evacuation to 10^{-3} mm. and admission of air did not alter the position of the plates.

Similar experiments with nitro-ethane vapour and with water vapour gave the same result. In no case was the behaviour of the plates different from that in air or vacua and there was no indication of the formation of long chains.

Experiments in Liquid.

Experiments were made with the plates completely immersed in liquid alcohol. As before, special precautions were taken to purify the alcohol and free it from dust. The plates were cleaned in dilute nitric acid, washed in water and alcohol and immersed in a flat glass dish full of alcohol. The larger plate was placed on the smaller while both were under the surface, and in this position could be viewed by sodium light or ordinary white light.

Almost immediately fine fringes were visible in sodium light; the top plate was probably 10 μ above the bottom plate and was sinking slowly. In about half a minute colour fringes were visible in white light indicating that the plates were less than 2 μ apart. In 3 minutes the bands had broadened, the first order violet being visible. The mean distance apart was roughly 0·75 μ. After this the descent was very slow.

When a 100 gm. weight was placed centrally on the top plate, it sank down till there were only second order fringes visible, with the first order yellow interference-colour showing at one corner, so that the minimum separation was less than 0·25 μ. On removing the 100 gm. weight there was no shift of the fringes and the top plate did not rise. When the alcohol was clean and free from dust the plates always sank down to this distance, but if the alcohol were contaminated with dust by exposure to the air the surfaces remained separated and no coloured fringes were visible.

By applying a very great pressure to the top plate and sliding it over the other, it was possible to decrease the mean distance apart to about 0·2 μ. The top plate was held by a pair of tweezers and pressed down with a force of about 3 kilogrammes. At the edges where the tweezers gripped, the plates showed silvery white interference colours (a separation of approximately 0·1 μ) and in the centre first order purple (approximately 0·27 μ). The plates were obviously distorted.

On releasing the pressure the edges of the top plate rose slightly giving purple interference colours and the centre of the plate fell giving first order amber colours (approximately 0·18 μ). The mean distance apart, however, remained practically the same. When the surfaces were first placed in contact (mean distance 0·36 μ) in air and then immersed in alcohol, the alcohol ran in between the plates, forcing out the air. If the air was not entrapped by the incoming alcohol, there was no rise of the top plate. If, however (and this was usually the case), the alcohol entered uniformly from all sides it imprisoned the air in the form of a square bubble, and compressed this to a smaller and smaller volume. Finally, the air pressure became too great, and the top plate suddenly broke away from the bottom plate, and lifted to a height of several microns, allowing the air bubble to escape. When the alcohol was dust-free, the top plate sank back again to its equilibrium position. If the alcohol were not dust-free, the two surfaces remained separated to a distance of several microns, supported by the solid particles which entered with the alcohol. The effect of a very thin film of alcohol spreading between the dry plates is to pull the surfaces more closely in contact. This force is very large, and can cause buckling of the thick glass plates. The behaviour when immersed in dust-free conductivity water was essentially the same.

These experiments argue against an oriented layer of liquid molecules extending to great distances from the surface, and support the recent work of Bulkley* on the viscosity of oils through fine capillaries. Bulkley has shown that the thickness of any immobile adsorbed layer of liquid cannot be greater than a few hundredths of a micron : the anomalous viscosities observed when the oils are not carefully filtered are due to dust sticking on the walls of the capillary.

Friction Experiments in Alcohol.

An attempt was made to measure the dependence of the static friction on the distance between the surfaces. A fine platinum wire was fastened round the edge of the top plate and attached to a light pan hanging over an almost frictionless pulley. The plates were placed together as before under the surface of the alcohol with a load of 100 gm. on the top plate and weights added to the pan until the top plate began to slide. The results are shown in the table.

Mean distance between plates.	Weight necessary to start sliding.
μ	gm.
ca. 10	$<0\cdot5$
2	$<0\cdot5$
1	$<0\cdot5$
0·5	$<0\cdot5$
0·36	40

The friction was very small (less than 0·5 gm. caused the plate to slide) until the plates were in very close contact. As the distance between the surface decreased from 10 μ to 0·5 μ the friction was too small to be measured. When the plates had sunk to their equilibrium position (0·36 μ) the friction rose to a high value. Approximately 40 gm. were required to start sliding. This is to be expected if the plate is sinking through free liquid until in its equilibrium position it is supported on solid particles.

Experiments made after the plates have been rubbed together under heavy pressure support this. The plates can now approach more closely together (to within 0·3 μ) before the friction becomes appreciable. Apparently the surface irregularities or dust particles have been ground down.

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* Bulkley, 'Bureau of Standards,' vol. 6, No. 1, p. 89, 1931.

Summary and Conclusion.

These experiments show that when a finely polished plate is lowered on to another polished surface in air, in vapour, or in liquid, the top plate will sink until the two surfaces are in close contact. The apparent "floating" at a height of 4 μ is due to dust or particles between the plates.

It is with great pleasure that we express our thanks for the assistance given us by Mr. A. S. C. Lawrence, whose detailed knowledge and experience of the colours of thin films have been invaluable.

The Viscosity of Dilute Solutions of Strong Electrolytes.

By W. E. Joy, B.A., B.Sc., Exeter College, Oxford, and J. H. Wolfenden, M.A., Fellow of Exeter College.

(Communicated by Sir Harold Hartley, F.R.S.—Received August 3, 1931.)

Introductory.

Until very recently, no empirical equation had been found to represent satisfactorily the variation with concentration of the relative viscosity of electrolytes, nor had any adequate theoretical treatment of the problem been put forward. In 1929, however, Jones and Dole* showed that the fluidity (or reciprocal of the relative viscosity) of a salt solution could be represented over a fairly wide range of concentration by an equation of the form

$$\phi = 1 + \mathrm{A}\sqrt{c} + \mathrm{B}c,$$

where ϕ is the fluidity, c the equivalent concentration, and A and B are empirical constants. The value of B is negative in the case of salts which increase the viscosity of water, and positive in cases of so-called "negative viscosity," where the viscosity of the solution is less than that of the pure solvent. Jones and Dole argued further that the stiffening effect of the interionic forces would tend to make the constant A, which determines the viscosity at high dilution, always negative. A little later, Falkenhagen and Dole† treated the problem theoretically from the standpoint of the ion-atmosphere theory of Debye and

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* 'J. Amer. Chem. Soc.,' vol. 51, p. 2950 (1929).

† 'Phys. Z.,' vol. 30, p. 611 (1929).

Huckel. They confirmed the suggestion that at high dilution the electrolyte must always increase the viscosity of the solvent, and showed that the relative viscosity of an electrolyte solution at high dilution must be represented by an equation of the form

$$\eta_\mu/\eta_0 = 1 + K\sqrt{\mu},$$

where

η_μ is the viscosity of the solution,
η_0 is the viscosity of the solvent,
μ is the equivalent concentration,
K is a constant.

For the special case of a binary electrolyte with ions of equal mobility, they found that the constant K must be given by the expression

$$K = \frac{e}{60\,\eta_0 u\sqrt{DkTz}} \times 0{\cdot}491 \times 10^{10}$$

where

e is the electronic charge,
η_0 is the viscosity of the solvent,
u is the reciprocal of the frictional force acting on the ions,
D is the dielectric constant of the solvent,
k is the Boltzmann constant,
T is the absolute temperature,
z is the valency of the ions.

For potassium chloride, the only salt whose ions have almost equal mobility in aqueous solution, the numerical value of K at 18° C. was calculated by Falkenhagen and Dole to be 0·0046. This is therefore the limiting slope to be expected when relative viscosity is plotted against the square root of the concentration at very high dilutions; with its sign changed it is of necessity also the theoretical value of A in the Jones-Dole equation.

A striking and unexpected feature of both these equations is that they predict that at sufficiently high dilution all electrolytes will raise the viscosity of the solvent, whereas it is well known that a number of salts of potassium, rubidium, and cæsium exhibit the phenomenon of "negative viscosity," that is to say, their solutions are less viscous than pure water. For example, at 18° C., the viscosity of aqueous solutions of potassium chloride at all concentrations hitherto measured is less than that of pure water. In only two of the recorded instances of negative viscosity is there any evidence that in dilute solution the viscosity is greater than that of pure water. The first instance is an isolated observation by Schneider,* who records a relative viscosity of 1·0008 for an N/20 solution of potassium chlorate, a salt which lowers the viscosity of water at higher concentrations. The second case is that of nitric acid. According to Bousfield,† the viscosity of nitric acid solutions at 11° C. is greater than unity up to a concentration of N/32, and less than unity at higher concentrations. His measurements at 4° C., however, indicate that the viscosity is less than unity at all concentrations, so that the initial increase of viscosity is peculiar to a certain range of temperature. The Falkenhagen-Dole equation predicts that the initial increase of viscosity must occur at all temperatures.

The first object of the present work was to make accurate measurements of the viscosity of potassium chloride solutions at high dilutions, to discover whether any concentration range existed where the viscosity of the solutions was greater than that of pure water and, if so, to compare the limiting slope of the viscosity-$\sqrt[2]{\text{concentration}}$ curve with the value predicted by the Falkenhagen-Dole equation. A preliminary announcement of the result of this investigation was communicated to ‘Nature.’‡

Since the work was begun, Falkenhagen§ has extended the theoretical treatment of the problem to the general case of the electrolyte with ions of any valency and mobility, and has derived a general equation. We have accordingly extended our measurements to three other electrolytes: potassium chlorate, rubidium nitrate, and nitric acid. Potassium chlorate was chosen because of the somewhat dubious observation by Schneider referred to above; rubidium nitrate was studied because the viscosity of its more concentrated solutions have already been measured in this laboratory ||; finally, nitric acid was chosen partly because of Bousfield's observations, and partly because the Falkenhagen equation predicts an unusually low value of K on account of the high mobility of the hydrion.

Experimental Method.

An adequate test of the theoretical predictions indicated above involves the measurement of viscosities at higher dilutions than any previously attempted.

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* “Dissertation,” Rostock (1910).

† ‘J. Chem. Soc.,’ vol. 107, p. 1781 (1915).

‡ Joy and Wolfenden, ‘Nature,’ vol. 126, p. 994 (1930).

§ ‘Z. Phys. Chem.,’ B, vol. 13, p. 93 (1931) and private communication. Since the communication of the present paper, the general equation has been published in ‘Phys. Z.,’ vol. 32, p. 745 (1931).

|| Smith, Wolfenden and Hartley, ‘J. Chem. Soc.,’ p. 403 (1931).

The limiting range in which the ideal conditions of the ionic atmosphere theory are realised is below N/100 in aqueous solution. At concentrations such as these the viscosity of an electrolyte never differs from that of the pure solvent by more than one part in a thousand. It was therefore necessary to measure the viscosity of the solutions with a precision of one part in ten thousand. To attain this end, various precautions and refinements of technique were necessary; these will now be described.

Viscometers.—The viscometers used were of the Washburn-Williams* type. Two (A and B) were made of Jena glass, while the other two (F and R) were made of silica. It was considered desirable to make measurements in both silica and glass in order to exclude the possibility of any systematic error arising from electrokinetic effects in the capillaries; no systematic difference was disclosed between the two types of viscometer, so that any effects of the type apprehended must lie within the experimental error of our measurements. In convenience and general concordance of results there was nothing to choose between the two types of viscometer.

The times of flow for water at 18° C. were, for A and B, 1750 and 1524 seconds respectively, and for F and R, 793 and 1057 seconds. The form and dimensions of all four viscometers conformed closely to the specifications of Washburn and Williams, who showed that viscometers of this design obey Poiseuille's law with great accuracy.

The viscometer holders were of the type first used by Applebey,† modified slightly so as to give extra support to the narrow limb of the viscometer.

Time Measurement.—Venner stop-watches with escapements making 30 beats per second were used. Three or four timings were carried out at any one concentration, and the extreme variation from the mean was usually about 0·05 second.

Temperature Control.—The viscometers were immersed in electrically controlled thermostats of some 40 litres capacity, which were vigorously stirred. The rates of heating and cooling were adjusted so that the heating and cooling periods were equal in length, amounting to about 50 seconds. Adjusted in this manner, the temperature of the thermostat varied regularly within the limits of 0·005° above and below the mean temperature. In view of the rhythmical character of the temperature variation, and the magnitude of the time of flow of the viscometers compared with that of the alternate heating and cooling periods, it can readily be shown that the maximum timing error due to casual temperature variations could not exceed 1/400 second.

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* 'J. Amer. Chem. Soc.,' vol. 35, p. 737 (1913).

† 'J. Chem. Soc.,' vol. 97, p. 2000 (1910).

In order to check continuously the effectiveness of the thermostatic control, a thermo-electric device was introduced which may be susceptible of extended application wherever it is desirable to detect or to estimate the minute temperature variations of a thermostat. For such a purpose the lag and "sticktion" of the average Beckmann thermometer make it a most misleading instrument by suggesting a constancy of temperature that may be far from the truth.

The present device consists of a multiple-junction thermel. The thermel consisted of 20 pairs of copper-constantan junctions; each set was embedded in naphthalene in a thin glass tube some 8 mm. in diameter. One set of junctions was immersed in the thermostat, while the other set were enclosed in a small Dewar vessel containing a quantity of paraffin, which was immersed in the thermostat. The first set of junctions records the variations of the temperature of the thermostat with a lag of 7 or 8 seconds. As soon as the Dewar vessel has taken up the temperature of the thermostat, the second set of junctions represents a constant temperature system which does not deviate from the mean temperature of the thermostat by as much as a ten-thousandth of a degree for many hours at a time.

If the thermel is connected to a fairly sensitive mirror galvanometer, the movements of the spot give a continuous record of the small variations of the temperature of the thermostat. The thermel used in the present work produced a deflection of 1 mm. for a temperature difference of 0·002°; this sensitivity was considered appropriate for the present work; it could, of course, be considerably increased. It is hardly necessary to say that both sets of junctions must be protected from direct radiation from any heating lamps used in the thermostat.

Method employed for Dilute Solutions.—The viscosity of the more dilute solutions was measured by a modification of the usual technique which ensured a degree of precision slightly higher than that usually achieved. The water-value was determined with the viscometer filled with 50 c.c. of water. A small volume of a concentrated solution was then added by means of a dropping pipette, fitted with a screw adjustment; the quantity added varied from 0·1 to 2 c.c., and could be measured to 0·01 c.c. The liquid in the viscometer was then thoroughly mixed, and the time of flow of the resultant solution measured in the ordinary way. A second and sometimes a third addition of concentrated solution was made in a similar manner. In this way the viscosity of two or three dilute solutions could be measured without emptying the viscometer.

The addition of a small quantity of solution alters the length of column of liquid in the viscometer, and consequently alters the time of flow. The necessary correction was made by calibrating each viscometer by the addition of similar small quantities of water, and measuring the increase in the time of flow per cubic centimetre of liquid added. Control experiments were also carried out to demonstrate that complete mixing was achieved after each addition.

The advantages of this " drop " method are that the viscometer is not dried out between the measurements of the times of flow of solvent and solution, that errors due to random variations in the volume delivered by the pipette used in filling the viscometer are eliminated, and that the highest degree of accuracy is most probable in the case of the most dilute solutions.

Materials.—The potassium chloride and chlorate and the rubidium nitrate used were the pure salts of Merck. Laboratory " pure " nitric acid was used without further purification. The solutions were made up with distilled water, which was filtered through Jena glass filters.

Results.

The relative viscosities of the solutions are calculated from the formula

$$\text{Relative viscosity} = \frac{t_s}{t_w} \times \frac{\Delta_{\text{solution}} - \Delta_{\text{air}}}{\Delta_{\text{water}} - \Delta_{\text{air}}},$$

where t_s is the time of flow of the solution after correction for the changed length of column.

The densities of the solutions were taken by interpolation from the following sources :—

Potassium chloride—
  At 18°, Lamb and Lee.*
  At 35°, Baxter.†

Rubidium nitrate—
  At 18°, Smith, Wolfenden, and Hartley (*loc. cit.*).
  At 35°, Clausen.‡

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* 'J. Amer. Chem. Soc.,' vol. 35, p. 1687 (1913).

† 'J. Amer. Chem. Soc.,' vol. 38, p. 70 (1916).

‡ 'Ann. Physik,' vol. 44, p. 1069 (1914).

Nitric acid—

At 18°, Bousfield.*

At 35°, Clausen.†

Potassium chlorate—

At 18°, Schneider (*loc. cit.*).

At 35°, determinations were made in the course of the present work.

No correction was applied for deviations from Poiseuille's law. This course is justified both by the known conformity of the Washburn-Williams type of viscometer with Poiseuille's law, and by the high dilution of nearly all the solutions, which made their viscosity almost identical with that of pure water. The latter consideration was also held to justify the omission of any surface tension correction.

The results for each salt are divided into two sections; the first section embodies the results obtained by the " drop " method, the second section those obtained with solutions made up directly beforehand. In every case the first column indicates the viscometer used, the second column the concentration of the solution in moles per litre, the third column the square root of the concentration, the fourth column the apparent relative density in air, the fifth column the relative viscosity, and the sixth column the Jones-Dole function $(\phi - 1)/\sqrt{c}$.

Potassium Chloride at 18° C.

Viscometer.	c.	$\sqrt{c}$.	Apparent relative density.	η/η_0.	$\phi - 1/\sqrt{c}$.
Solutions made up by the " drop " method.					
A	0·00198	0·0445	1·00009	1·00016	—0·0036
B	0·00398	0·0631	1·00020	1·00021	—0·0033
R	0·00407	0·0638	1·00020	1·00029	—0·0045
R	0·00646	0·0804	1·00032	1·00026	—0·0032
B	0·00715	0·0845	1·00035	1·00021	—0·0025
B	0·01186	0·1088	1·00057	1·00018	—0·0017
R	0·01192	0·1092	1·00058	1·00019	—0·0018
B	0·01789	0·1338	1·00086	1·00014	—0·0010
R	0·01807	0·1344	1·00087	0·99999	0·0000
R	0·02299	0·1516	1·00111	0·99999	0·0000
R	0·02344	0·1531	1·00114	1·00005	—0·0003
B	0·03138	0·1771	1·00152	0·99991	0·0005
A	0·03846	0·1961	1·00186	0·99977	0·0012
B	0·03846	0·1961	1·00186	0·99989	0·0006
B	0·03865	0·1966	1·00187	0·99974	0·0013
R	0·03883	0·1971	1·00188	0·99956	0·0022
B	0·06458	0·2542	1·00312	0·99920	0·0031
B	0·10033	0·3167	1·00481	0·99854	0·0046

* 'J. Chem. Soc.,' vol. 107, p. 1405 (1915).

† 'Ann. Physik,' vol. 37, p. 64 (1912).

Potassium Chloride at 18° C.—(continued).

Viscometer.	c.	$\sqrt{c}$.	Apparent relative density.	η/η_0.	$\phi - 1/\sqrt{c}$.
Solutions made up directly.					
R	0·1000	0·3162	1·00480	0·99837	0·0052
F	0·1000	0·3162	1·00480	0·99840	0·0051
R	0·2500	0·5000	1·01187	0·99496	0·0101
F	0·2500	0·5000	1·01187	0·99484	0·0104
R	0·5000	0·7071	1·02359	0·98979	0·0146
R	1·0000	1·0000	1·0464	0·9823	0·0180

Potassium Chloride at 35° C.

Viscometer.	c.	$\sqrt{c}$.	Apparent relative density.	η/η_0.	$\phi - 1/\sqrt{c}$.
Solutions made up by the "drop" method.					
B	0·00398	0·0631	1·00019	1·00032	−0·0050
A	0·00398	0·0631	1·00019	1·00032	−0·0050
F	0·00398	0·0631	1·00019	1·00041	−0·0065
A	0·00794	0·0891	1·00037	1·00045	−0·0050
B	0·01186	0·1089	1·00056	1·00059	−0·0055
A	0·01186	0·1089	1·00056	1·00059	−0·0055
F	0·01575	0·1255	1·00074	1·00081	−0·0065
B	0·01575	0·1255	1·00074	1·00082	−0·0065
A	0·02645	0·1627	1·00124	1·00111	−0·0068
R	0·02645	0·1627	1·00124	1·00096	−0·0059
F	0·02645	0·1627	1·00124	1·00100	−0·0062
A	0·03101	0·1761	1·00145	1·00105	−0·0060
A	0·06536	0·2556	1·00306	1·00199	−0·0078
R	0·06536	0·2556	1·00306	1·00192	−0·0075
F	0·06536	0·2556	1·00306	1·00193	−0·0075
A	0·11583	0·3403	1·00542	1·00287	−0·0084
F	0·11583	0·3403	1·00542	1·00273	−0·0080
Solutions made up directly.					
F	0·5000	0·7071	1·02295	1·0078	−0·0109
R	0·5000	0·7071	1·02295	1·0078	−0·0109
F	0·7500	0·8660	1·03410	1·0112	−0·0128
F	1·0000	1·0000	1·04520	1·0154	−0·0152

Nitric Acid at 18° C.

Viscometer.	c.	$\sqrt{c}$.	Apparent relative density.	η/η_0.	$\phi - 1/\sqrt{c}$.
Solutions made up by the "drop" method.					
A	0·00994	0·0997	1·00034	1·00027	—0·0027
A	0·01035	0·1017	1·00035	1·00029	—0·0029
F	0·02060	0·1435	1·00069	1·00055	—0·0038
R	0·02060	0·1435	1·00069	1·00040	—0·0028
A	0·04078	0·2019	1·00137	1·00067	—0·0035
A	0·04245	0·2060	1·00143	1·00083	—0·0040
F	0·06058	0·2461	1·00205	1·00117	—0·0048
R	0·06058	0·2461	1·00205	1·00088	—0·0036
A	0·10146	0·3185	1·00346	1·00149	—0·0047
B	0·10146	0·3185	1·00346	1·00148	—0·0047
Solutions made up directly.					
F	0·4440	0·6663	1·01510	1·00559	—0·0083
R	0·4440	0·6663	1·01510	1·00564	—0·0084
F	1·110	1·054	1·03776	1·01878	—0·0175
R	1·110	1·054	1·03776	1·01878	—0·0175

Nitric Acid at 35° C.

Viscometer.	c.	$\sqrt{c}$.	Apparent relative density.	η/η_0.	$\phi - 1/\sqrt{c}$.
Solutions made up by the "drop" method.					
A	0·00994	0·0997	1·00032	1·00053	—0·0053
A	0·00994	0·0997	1·00032	1·00059	—0·0059
B	0·00994	0·0997	1·00032	1·00057	—0·0057
B	0·04078	0·2019	1·00132	1·00194	—0·0096
A	0·04078	0·2019	1·00132	1·00202	—0·0100
A	0·04234	0·2058	1·00138	1·00187	—0·0091
R	0·08615	0·2935	1·00282	1·00391	—0·0133
B	0·10146	0·3185	1·00331	1·00427	—0·0134
A	0·10146	0·3185	1·00331	1·00433	—0·0136
Solutions made up directly.					
R	0·560	0·748	1·01839	1·0221	—0·0290
A	0·560	0·748	1·01839	1·0223	—0·0291
R	1·120	1·058	1·03678	1·0476	—0·0430

Rubidium Nitrate at 18° C.

Viscometer.	c.	$\sqrt{c}$.	Apparent relative density.	η/η_0.	$\phi - 1/\sqrt{c}$.
Solutions made up by the " drop " method.					
R	0·00199	0·0446	1·00021	1·00002	−0·0004
R	0·00495	0·0704	1·00052	0·99981	0·0027
Solutions made up directly.					
F	0·01000	0·1000	1·00105	0·99931	0·0069
F	0·01000	0·1000	1·00105	0·99941	0·0059
R	0·01000	0·1000	1·00105	0·99938	0·0062
R	0·01000	0·1000	1·00105	0·99934	0·0066
F	0·02000	0·1414	1·00210	0·99845	0·0110
R	0·02000	0·1414	1·00210	0·99846	0·0109
F	0·05000	0·2236	1·00525	0·99581	0·0188
R	0·05000	0·2236	1·00525	0·99584	0·0187
F	0·10000	0·3162	1·01044	0·99159	0·0268
R	0·10000	0·3162	1·01044	0·99155	0·0269

Rubidium Nitrate at 35° C.

Viscometer.	c.	$\sqrt{c}$.	Apparent relative density.	η/η_0.	$\phi - 1/\sqrt{c}$.
Solutions made up by the " drop " method.					
A	0·00259	0·0509	1·00027	1·00015	−0·0030
B	0·00259	0·0509	1·00027	1·00017	−0·0034
A	0·00775	0·0880	1·00079	1·00013	−0·0015
B	0·00794	0·0891	1·00081	1·00009	−0·0010
A	0·00794	0·0891	1·00081	1·00024	−0·0027
B	0·02204	0·1485	1·00226	0·99976	0·0016
A	0·02204	0·1485	1·00226	0·99986	0·0009
A	0·02344	0·1531	1·00240	0·99989	0·0007
A	0·03846	0·1961	1·00394	0·99932	0·0035
B	0·03846	0·1961	1·00394	0·99933	0·0034
Solutions made up directly.					
B	0·1000	0·3162	1·01025	0·99704	0·0094
A	0·1000	0·3162	1·01025	0·99694	0·0097
F	0·2500	0·5000	1·02551	0·9927	0·0147
A	0·5000	0·7071	1·05095	0·9858	0·0204
A	0·5000	0·7071	1·05095	0·9856	0·0206
F	1·0000	1·0000	1·10100	0·9800	0·0204

Potassium Chlorate at 18° C.

Viscometer.	c.	$\sqrt{c}$.	Apparent relative density.	η/η_0.	$\phi - 1/\sqrt{c}$.
Solutions made up by the "drop" method.					
F	0·00124	0·0353	1·00010	1·00015	−0·0042
R	0·00124	0·0353	1·00010	1·00013	−0·0037
F	0·00490	0·0700	1·00038	1·00004	−0·0006
R	0·00490	0·0700	1·00038	1·00006	−0·0008
Solutions made up directly.					
F	0·01000	0·1000	1·00078	0·99993	0·0007
R	0·01000	0·1000	1·00078	0·99993	0·0007
R	0·02000	0·1414	1·00155	0·99956	0·0031
R	0·02000	0·1414	1·00155	0·99958	0·0030
R	0·04000	0·2000	1·00310	0·99871	0·0064
R	0·04000	0·2000	1·00310	0·99874	0·0063
R	0·04000	0·2000	1·00310	0·99879	0·0060
F	0·06250	0·2500	1·00483	0·99786	0·0086
R	0·06250	0·2500	1·00483	0·99785	0·0086
F	0·12500	0·3536	1·00966	0·99524	0·0135
R	0·12500	0·3536	1·00966	0·99529	0·0135
F	0·25000	0·5000	1·01932	0·99082	0·0185
R	0·25000	0·5000	1·01932	0·99090	0·0184
F	0·40000	0·6325	1·03104	0·98706	0·0207
R	0·40000	0·6325	1·03104	0·98716	0·0206

Potassium Chlorate at 35° C.

Viscometer.	c.	$\sqrt{c}$.	Apparent relative density.	η/η_0.	$\phi - 1/\sqrt{c}$.
Solutions made up by the "drop" method.					
A	0·00238	0·0488	1·00018	1·00018	−0·0037
B	0·00442	0·0665	1·00034	1·00032	−0·0048
A	0·00442	0·0665	1·00034	1·00027	−0·0041
B	0·00869	0·0932	1·00065	1·00050	−0·0053
A	0·00869	0·0932	1·00065	1·00043	−0·0046
A	0·00869	0·0932	1·00065	1·00043	−0·0046
Solutions made up directly.					
B	0·02000	0·1414	1·00150	1·00060	−0·0043
A	0·02000	0·1414	1·00150	1·00067	−0·0047
R	0·02000	0·1414	1·00150	1·00057	−0·0040
R	0·04000	0·2000	1·00300	1·00080	−0·0040
R	0·04000	0·2000	1·00300	1·00085	−0·0042
B	0·04000	0·2000	1·00300	1·00070	−0·0035
A	0·04000	0·2000	1·00300	1·00084	−0·0042
R	0·10000	0·3162	1·00750	1·00116	−0·0037
R	0·10000	0·3162	1·00750	1·00111	−0·0035
A	0·10000	0·3162	1·00750	1·00114	−0·0036
R	0·16000	0·4000	1·01200	1·00156	−0·0039
B	0·16000	0·4000	1·01200	1·00150	−0·0037
B	0·16000	0·4000	1·01200	1·00145	−0·0036
A	0·16000	0·4000	1·01200	1·00133	−0·0033
R	0·25000	0·5000	1·01864	1·00175	−0·0035
R	0·40000	0·6325	1·02984	1·00328	−0·0052

Discussion of Results.

The results tabulated above and illustrated in figs. 1, 2 and 3 are in complete agreement with the predictions of the ionic atmosphere theory. In all three salts showing negative viscosity at ordinary concentrations it will be seen that the most dilute solutions are more viscous than pure water.

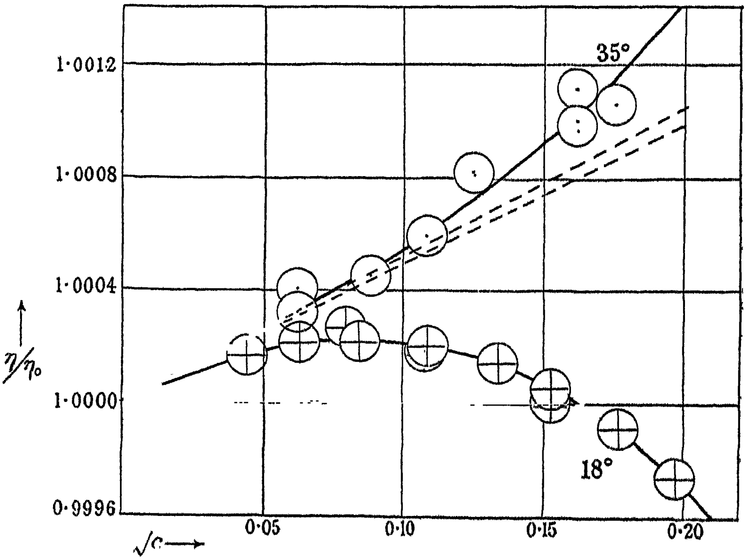

FIG. 1.—Relative viscosity of potassium chloride solutions at 18° and 35° C. (The dotted lines represent the theoretical limiting slopes.)

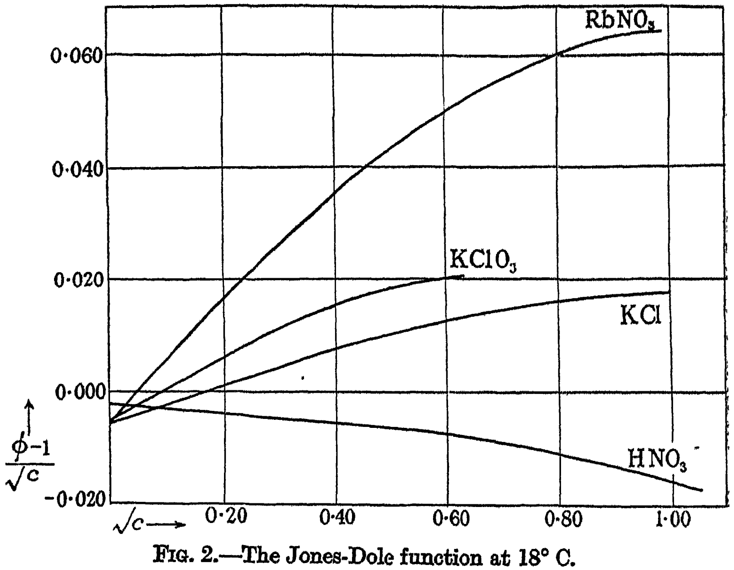

FIG. 2.—The Jones-Dole function at 18° C.

Quantitatively the concordance with theory is equally striking. The coefficient K of the Falkenhagen equation is most conveniently determined from the intercept of the function $(\phi - 1)/\sqrt{c}$ on the axis of zero concentration. The following table sets out the experimental values at both temperatures side by side with the theoretical values calculated from the equation. Except for a relatively small discrepancy for potassium chlorate at the higher temperature, the theoretical and experimental values agree, within the experimental error, in every case.

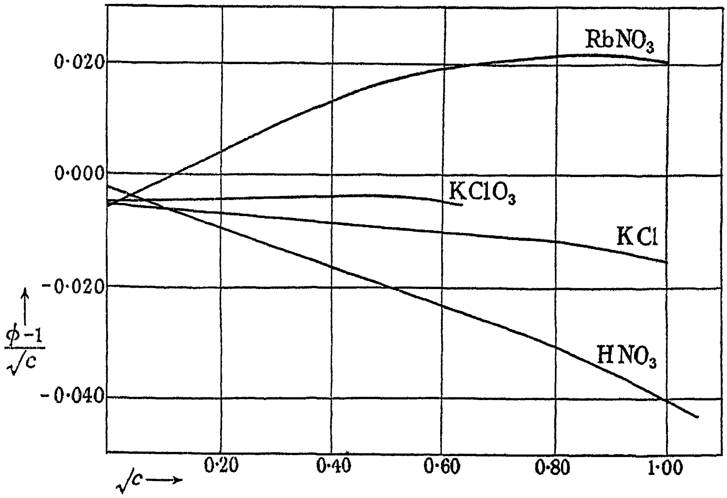

FIG. 3.—The Jones-Dole function at 35° C.

	A18° theoretical.	A18° experimental.	A35° theoretical.	A35° experimental.
KCl	0·0049	0·0052 ±0·0005	0·0052	0·0051 ±0·0005
HNO_3	0·0021	0·0021 ±0·0005	0·0025	0·0023 ±0·0005
$RbNO_3$	0·0049	0·0050 ±0·0005	0·0054	0·0056 ±0·0005
$KClO_3$	0·0052	0·0050 ±0·0005	0·0058	0·0049 ±0·0005

The variation of K with temperature is within the experimental error. This is to be anticipated from the equation, since the variations of D and T between 18° and 35° are both small, and D decreases as T increases. The variations of D are rather larger than those of T, so that the effect of an increase of temperature is to cause a small increase in the value of K. Falkenhagen and Dole seem to have overlooked the variation of D with temperature in their original paper, where they state that the marked diminution in K with rise of temperature suggested by Merton's results for cæsium nitrate is in accordance with the theoretical equation. It seems more likely that in this case, and in that of rubidium nitrate,* an erroneously high temperature coefficient for K has been obtained by extrapolation from measurements made at too high concentrations.

The Jones-Dole Equation.—The range of validity of this equation, the forerunner of the theoretical treatment, varies considerably from one electrolyte to another. As its authors have suggested, the range is markedly less for electrolytes showing negative viscosity than for those whose viscosity is always greater than that of pure water. Related to this, no doubt, is the fact that deviations from the equation begin at lower concentrations at 18° C. than at 35° C. The deviations are always in the sense that the viscosity of the most concentrated solutions is greater than the value predicted by the equation.

Below are given the most probable values for the coefficients A and B, together with a rough estimate of the concentration up to which the equation is valid in each case.

	18° C.		Limiting concentration.	35° C.		Limiting concentration.
	A.	B.		A.	B.	
$RbNO_3$	−0·0050	0·1120	0·02 N	−0·0056	0·0470	0·10 N
$KClO_3$	−0·0050	0·0560	0·07 N	−0·0049	0·0035	0·15 N
KCl	−0·0052	0·0330	0·15 N	−0·0051	−0·0090	0·50 N
HNO_3	−0·0021	−0·0080	0·25 N	−0·0023	−0·0365	0·60 N

The correlation between the value of B and the range of validity of the Jones-Dole equation is quite regular. The change of sign of the B coefficient of potassium chloride with rising temperature is striking; the relative viscosity of potassium chloride solutions at 35° C. is always greater than unity. The results for potassium chlorate show quite conclusively that Schneider's value of 1·0008 for the relative viscosity of an N/20 solution at 18° C. is much in error; according to the present experiments the relative viscosity of potassium chlorate solutions is less than unity until the concentration falls below about N/100.

Summary.

(1) The viscosity of aqueous solutions of potassium chloride, potassium chlorate, rubidium nitrate, and nitric acid have been measured at 18° C. and 35° C. over the range of concentration N to 0·002 N.

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* Smith, Wolfenden and Hartley, *loc. cit.*

(2) The viscosity of all these solutions at high dilution is greater than that of pure water, in agreement with the prediction of Jones and Dole. The limiting slopes of the viscosity-concentration curves and their temperature coefficients agree, within the experimental error, with the values predicted by the Falkenhagen-Dole equation. The confirmation of the ionic-atmosphere theory of strong electrolytes has thus been extended to a further property of electrolyte solutions.

We wish to express our thanks to the Directors of Imperial Chemical Industries, Ltd., for grants which defrayed the cost of part of the apparatus used in this investigation.

Photo-Electrons and Negative Ions.

By E. M. Wellish, M.A., University of Sydney.

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1. *Introduction.*

The normal law connecting the mobility (k) of a gas ion with the pressure (p) of the gas, is that the product pk is constant. More than 20 years ago Kovarik* found that this product showed an abnormal increase in the case of the negative ions formed in air and carbon dioxide when the pressure was lowered below 20 cm. approximately; this result was interpreted as denoting a progressive diminution in the size and mass of the ion as the pressure is reduced.

Some years later† the author conducted an experimental investigation, from the results of which he concluded that at the lower pressures the carriers of negative electricity consist of two kinds, electrons and ions; the electrons come more and more into evidence as the pressure of the gas is reduced and travel freely under the influence of an applied field without becoming attached to molecules. From this point of view anomalous mobilities will be obtained at lower pressures unless the electrons are separated experimentally from the negative ions. The author found that, when this separation was effected, the mobility law, $pk =$ const., remained valid down to the lowest pressure employed, viz., 0·15 mm.

* 'Phys. Rev.,' vol. 30, p. 415 (1910).

† 'Amer. J. Sci.,' vol. 39, p. 583 (1915).

This explanation of the anomalous mobilities of the negative ions was at first well received, but was superseded by a theory advanced about the same time by Sir J. J. Thomson.* The assumption underlying this theory is that the carriers of negative electricity originate as electrons which at lower pressures can travel considerable distances in the free state before becoming attached to molecules of the gas and thus giving rise to negative ions; out of n collisions of an electron with the molecules, on the average only one will result in the formation of an ion. Sir J. J. Thomson regarded n as a constant for the given gas, independent of the pressure and the applied field. Loeb assigned to n the value $2 \cdot 5 \times 10^5$ for pure dry air.

The attachment of electrons to gas molecules has been made the subject of careful study by Professor V. A. Bailey and his associates, who have investigated the process in various gases and have in addition formulated a mathematical theory. In this theory there is introduced, instead of the constant n, a symbol (α) denoting the probability of attachment per unit distance as the electron moves through the gas in the direction of the applied field (X); this probability is such that α/p is a function of X/p. The probability of attachment at a collision is expressed by a symbol (h) which is functionally related to α.

In 1921 Loeb† undertook an experimental investigation in order to explain the phenomenon of anomalous mobilities. He came to the conclusion that his experimental results, as well as those obtained previously by the author, could be explained quantitatively on the theory advanced by Sir J. J. Thomson. This conclusion was based chiefly on considerations with regard to a special type of curve exhibiting the current obtained when the carriers of negative electricity are subjected to an alternating potential difference of "square" wave form. This type of curve, reproduced in fig. 1, had led the author to the explanation previously given; the component marked I is undoubtedly due to negative ions which have traversed the whole distance between the electrodes and that marked E was ascribed to free electrons.

Loeb found that this characteristic type of curve presented itself only when there was an antechamber in which the electrons were generated; such an antechamber formed part of the measuring vessel employed by the author. Loeb ascribed the I component to negative ions resulting from the attachment of electrons to molecules in the antechamber; while the E components of the curves which he obtained reproduced the features of those obtained by Kovarik and were ascribed to carriers starting as electrons, passing through the meshes of a gauze partition, and then becoming attached to molecules in the measuring field.

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* 'Phil. Mag.,' vol. 30. p. 321 (1915).

† 'Phys. Rev.,' vol. 17, p. 89 (1921).

Loeb's experiment appeared to be decisive. But there were certain considerations which decided the author to make a closer investigation if an opportunity occurred to do so. Such an opportunity presented itself when the Mathematical Department was transferred to new quarters in the Physics Laboratory. Facilities were available for experimental research, and an investigation was commenced the original purpose of which was to ascertain whether a characteristic curve with E and I components was obtainable in a measuring vessel of the parallel plate type without gauze or antechamber.

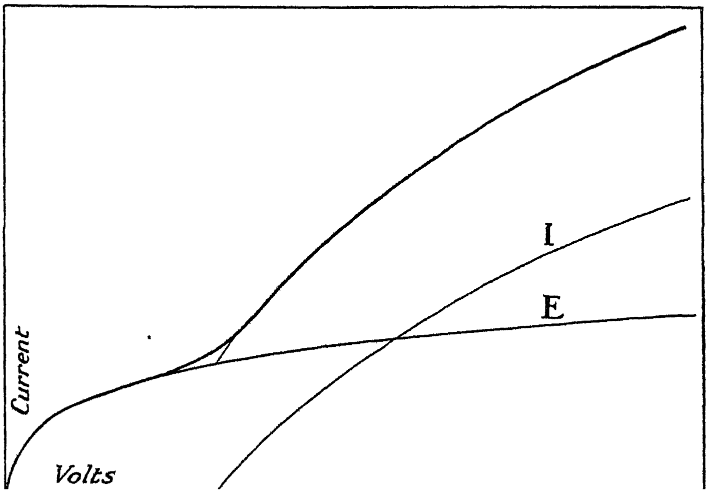

FIG. 1.

2. *Experimental Arrangement.*

In the previous experiment conducted by the author the air was ionised by means of alpha particles emitted from a deposit of polonium. The effect of the gauze was that the carriers of electricity which entered the measuring field traversed the whole distance between the electrodes. As it was decided to dispense with the gauze partition it was practically essential that the carriers should originate in the vicinity of one of the electrodes. On this account the electric carriers were generated by means of light proceeding from a quartz mercury vapour lamp and incident on one of the electrodes of the measuring vessel. The lamp employed was a "Home Sun," D.C. type, provided with a protective screen and adjustable apertures ; it worked nominally on 110 volts, but with this voltage the screen caused superheating and the working voltage was reduced to 60. The light passed through two quartz lenses and a quartz window into the measuring vessel and after incidence on the electrode emerged through a second quartz window. The interior of the vessel was oxidised in order to minimise the effects of scattered radiation ; any residual effect due to this cause was always measured and a corresponding correction was made in the experimental observations.

The diagram of connections is shown in fig. 2. The measuring vessel A consisted essentially of a brass cylinder containing two gold-plated circular electrodes distant 2 cm. apart ; the upper electrode (6 cm. in diameter) was provided with a guard ring. Two tapered quartz plugs were used as insulators.

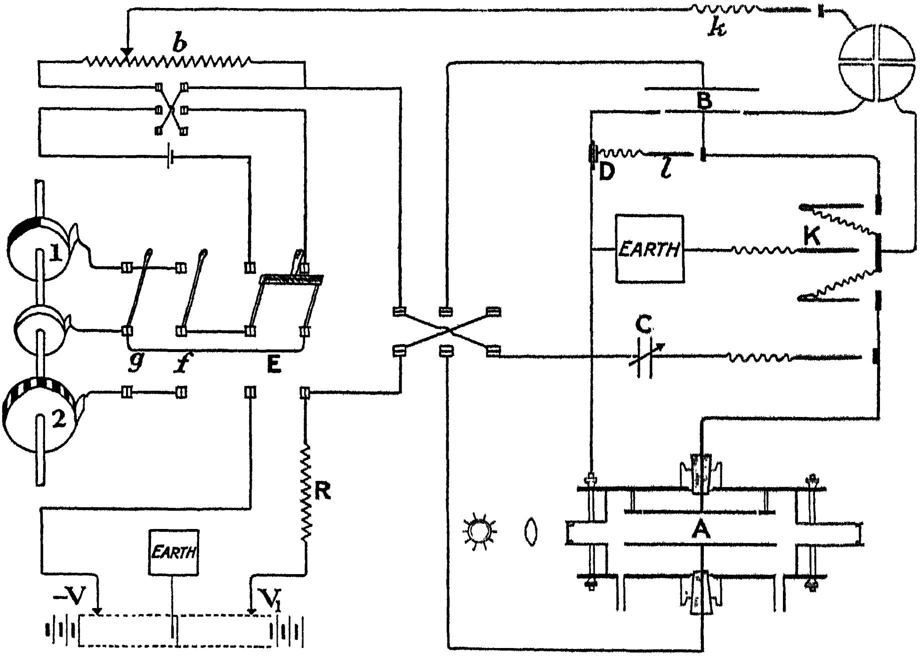

Fig. 2.

The gas employed throughout the experiment was air ; before entering the measuring vessel the air was dried by passage through a tube containing calcium chloride, and three tubes in series each containing phosphorus pentoxide. A Cenco Megavac pump was used for evacuation and pressures were read by mean of a baromanometer and a McLeod gauge.

The diagram illustrates the method employed to effect the commutation of potential. The commutator was the same instrument as used in the previous investigations; it had two commutating discs, one with 20 equally spaced fibre segments, and the other half fibre and half metal. One brush was used on the low frequency disc (1), two brushes on the collector ring, and three on the high frequency disc (2). The commutator was actuated by means of an A.C. single-phase induction motor, and a speed counter was attached permanently to the shaft. When the brushes are in metallic contact with a commutating disc the lower electrode of A has a potential —V; when the contact is broken a potential V_1 is established through the resistance R. If R is not excessively great an alternating potential difference of "square" wave form will be approximately realised; the values of R employed varied from 20,000 to 100,000 ohms according to circumstances, and tests were made throughout to ensure an effectively instantaneous establishment of the retarding potential V_1. The electric carriers in the gas advance to the receiving electrode during a fraction (f) of the time of a complete cycle; in the remainder of the cycle those which fail to reach this electrode will be withdrawn from the gas if V_1 is sufficiently great. When disc 1 was employed f was almost exactly 0·5; with disc 2, owing to difference in the lengths of the brushes, the value of f was greater. The source of potential was a battery of nickel-iron accumulators.

In the diagram B is a parallel-plate condenser used for purposes of calibration; C is a condenser whose capacity was variable to 0·0005 mf. and which was employed to reduce the maximum rate of deflection of the electrometer needle to a suitable value. The potentiometer system *b* actuated by the key *k* was employed: (i) to test the nature of the contact between the brushes and the commutating discs; (ii) to check values of f which were usually deduced from the experimental curves; (iii) to control the throw of the electrometer needle which invariably occurred on insulating the system with the commutator in action.

D is a mica condenser (0·5 mf.) actuated by the key *l* and used solely to absorb the electricity liberated when the switch E was thrown. The electrometer was of the Dolezalek type with quartz insulation, having a sensitivity of 375 mm. per volt on a scale about 1 m. distant.

3. *Initial Procedure and Results.*

The first series of experiments consisted in obtaining curves expressing the current registered by the electrometer for different values of the potential V. Such curves were obtained for various pressures and for both high and low frequencies. At the outset there were indications of curves with E and I components, but these proved to be due to unsteadiness in the source of light. When the lamp was allowed to burn for 30 minutes before readings were commenced the light emission became constant; under these circumstances a normal type of curve was obtained. An example is given in fig. 3 which relates to a pressure of 59 mm.; the curve i_2 corresponds to the higher frequency (n_2) of commutation, that marked i_0 to a steady difference of potential, while the third curve gives the ratio i_2/i_0.

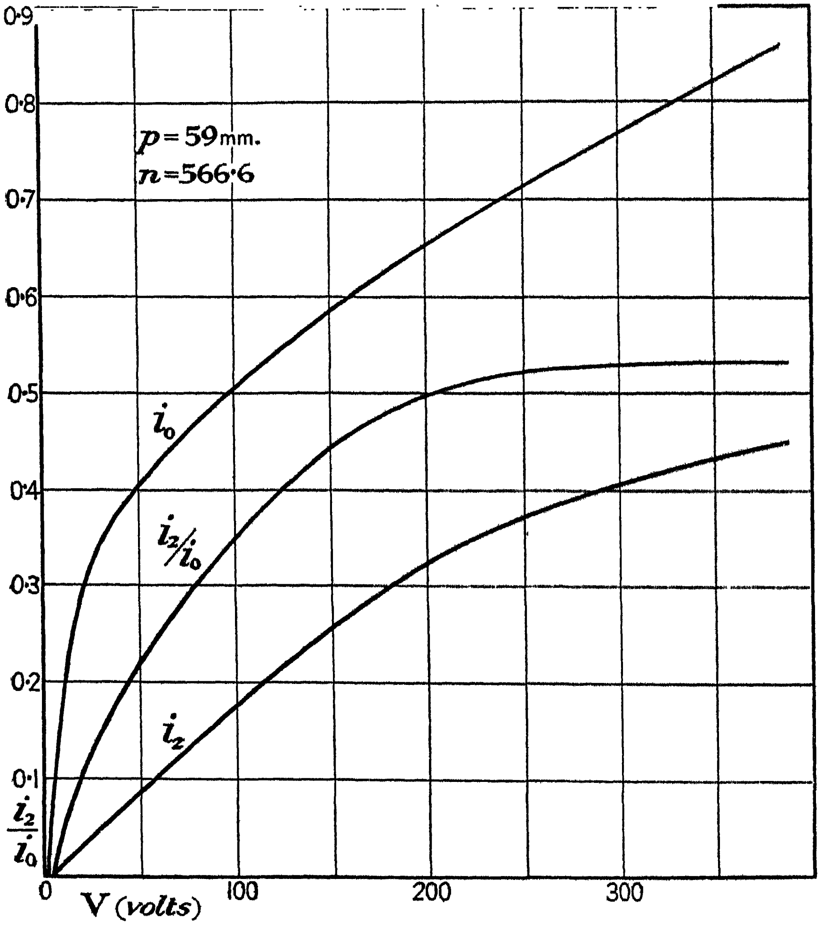

FIG. 3.

The absence of a typical EI curve was in agreement with the experimental observations of Loeb, and appeared to necessitate the interpretation which he had already given, viz., that the negative ions are formed by the attachment of electrons to molecules in their passage through the gas.

4. *Subsequent Procedure and Results.*

The investigation was resumed with the object of obtaining information concerning the process involved in the formation of negative ions. It was necessary to modify the procedure because that originally adopted did not appear promising. It was decided to replace V by 1/V in plotting the experimental curves; this course was indicated by the consideration that a rectilinear graph is obtained when the carriers possess a definite mobility. As ordinate the ratio i/i_0 was chosen instead of i in order to eliminate the effect of small irregularities and unsteadiness in the source of radiation. This procedure had previously been adopted by Hamshere.*

In the experimental observations for any given pressure the current (i_0) due to a steady potential was taken, also the currents (i_1 and i_2) corresponding to the low and high frequencies of commutation. The potential was then varied and the procedure repeated until sufficient data for a complete set of curves were available. The values of i_1, i_2, i_0 were then plotted against V; the ratios i_1/i_0, i_2/i_0 were plotted firstly against V and finally against 1/V.

Examples of the curves obtained are given in figs. 4 and 5. The values of n,

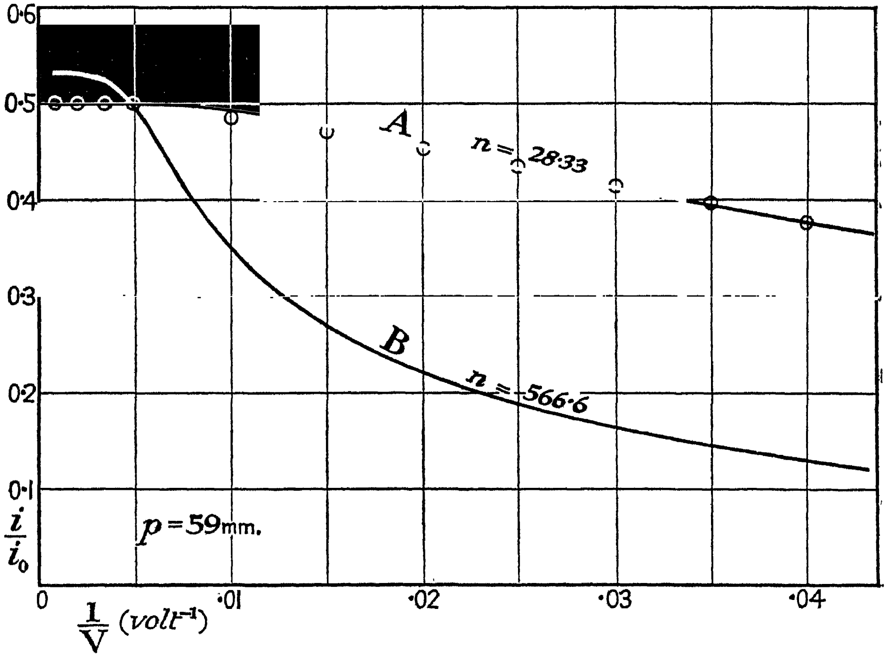

Fig. 4.

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* 'Proc. Roy. Soc.,' A, vol. 127, p. 298 (1930).

the number of complete cycles per second, are indicated on each curve. Fig. 4 exhibits the type of curve obtained when the current ratios are plotted against the reciprocal of the advancing potential; in both curves of this diagram there are flat portions corresponding to the larger potentials, while in curve B which refers to the higher frequency there is apparently a point of inflexion. It was significant that this point of inflexion always corresponded to the voltage which was required in order that the negative ions proceeding from the lower plate should just reach the receiving electrode.

To interpret these curves it was essential to obtain a mathematical expression for i/i_0 as a function of V; the development would necessarily include an assumption regarding the mode of formation of the negative ions.

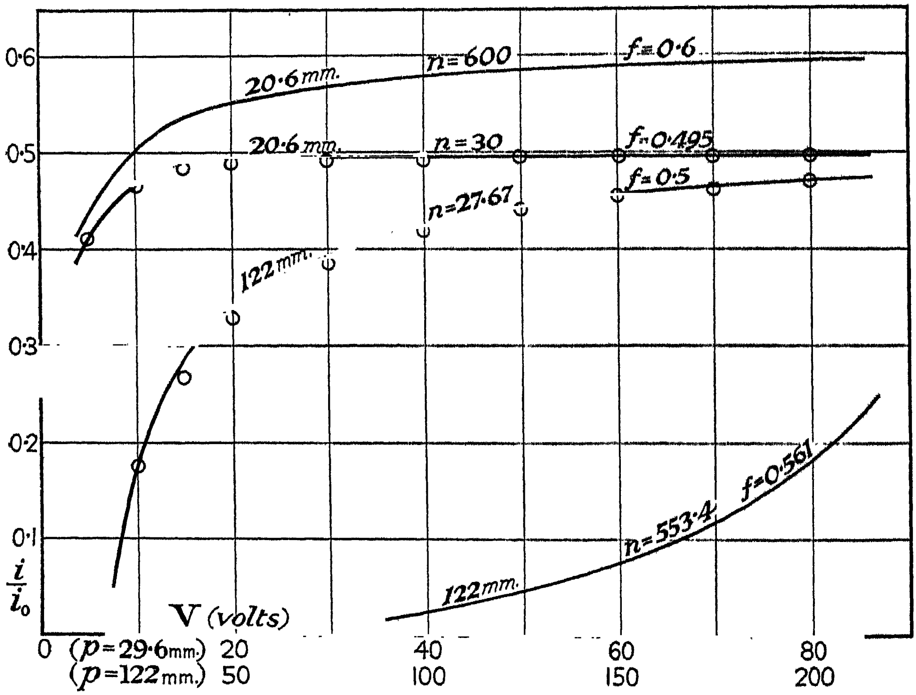

Fig. 5.

5. *Mathematical Theory and Application.*

The assumption is first made that the electric carriers are formed as electrons in the vicinity of the lower electrode and that a fraction of these become attached to molecules during their passage through the gas, thus giving rise to the negative ions.

Let N_0 electrons be produced per second at the lower plate. Owing to attachments N electrons will arrive per second at the plane distant x from the lower plate.

Suppose $N + dN$ electrons pass per second in the free state through the plane distant $x + dx$. Then $dN = - \lambda N dx$, where λ depends on the nature of the gas and is in general a function of the advancing potential V and the pressure p. Integrating

$$N = N_0 e^{-\lambda x}.$$

Suppose the commutator generates a potential difference of square wave form. Let the advancing phase occupy a fraction f of the total time, so that in each cycle it is established for f/n second where n is the number of complete cycles per second. We will suppose that the drift velocity of the electrons is large compared with that of the ions and disregard the time taken by the electrons to traverse any portion of the distance between the electrodes. When the advancing phase commences all ions and electrons will have been removed from the measuring field.

Out of N_0 electrons which are produced per second at the lower plate $\lambda N_0 e^{-\lambda x} dx$ ions will be formed by attachment in the layer x, $x + dx$. These negative ions will occupy a time $d\,(d - x)/kV$ in arriving at the upper plate, k being the ionic mobility and d the distance between the electrodes.

Considering only one complete cycle the upper electrode will receive from the x, $x + dx$ layer those ions which have originated as electrons at the lower plate during an interval $\frac{f}{n} - \frac{d\,(d - x)}{kV}$, and which have been subsequently formed by attachment in this layer. This will be valid provided $\frac{f}{n} - \frac{d\,(d - x)}{kV}$ is positive, *i.e.*, if $V > \frac{nd\,(d - x)}{fk}$.

Now $\lambda N_0 e^{-\lambda x} dx$ ions are formed per second in this layer; hence the number of ions received per cycle by the upper electrode from all layers when the commutator is in action is

$$\int_0^d \left\{ \frac{f}{n} - \frac{d\,(d - x)}{kV} \right\} \lambda N_0 e^{-\lambda x} dx.$$

The number of free electrons received per cycle is $(f/n) e^{-\lambda d} N_0$. If a steady potential V were applied to the lower plate for the time of one cycle the number of carriers received would be N_0/n.

Thus if i denote the current registered by the electrometer when the commutator is in action and i_0 the steady current, we will have

$$\frac{i}{i_0} = n\left[\int_0^d \left\{\frac{f}{n} - \frac{d\,(d-x)}{k\mathrm{V}}\right\}\lambda e^{-\lambda x}\,dx + \frac{f}{n}e^{-\lambda d}\right]. \tag{i}$$

If $\mathrm{V} > nd^2/fk$, then, *a fortiori*, $\mathrm{V} > nd\,(d-x)/fk$ for $0 < x < d$.

Thus the above considerations will be valid for values of V greater than nd^2/fk. But if $\mathrm{V} < nd^2/fk$, there will be a range of layers x, $x + dx$ so situated that ions formed by attachment in these layers will not be received at the upper plate before the field is reversed.

Suppose that for a particular value of V ($< nd^2/fk$) those ions can just be received which proceed from a distance ξ measured from the lower plate. Then

$$\frac{f}{n} = \frac{d-\xi}{k\mathrm{V}/d} \quad \text{or} \quad \mathrm{V} = \frac{nd\,(d-\xi)}{fk}.$$

Thus, for values of V ranging from 0 to nd^2/fk we will have

$$\frac{i}{i_0} = n\left[\int_\xi^d \left\{\frac{f}{n} - \frac{d\,(d-x)}{k\mathrm{V}}\right\}\lambda e^{-\lambda x}\,dx + \frac{f}{n}e^{-\lambda d}\right]. \tag{ii}$$

To evaluate the integrals contained in (i) and (ii) we use the results

$$\int_\xi^d \lambda e^{-\lambda x}\,dx = e^{-\lambda\xi} - e^{-\lambda d}$$

$$\int_\xi^d \lambda x e^{-\lambda x}\,dx = \left(\frac{1}{\lambda} + \xi\right)e^{-\lambda\xi} - \left(\frac{1}{\lambda} + d\right)e^{-\lambda d}$$

Substituting these values and putting

$$\xi = d - \frac{fk}{nd}\mathrm{V}$$

we obtain

$$\frac{i}{i_0} = f - \frac{nd}{k\mathrm{V}}\left\{d - \frac{1}{\lambda}\,(1 - e^{-\lambda d})\right\} \qquad \left(\mathrm{V} > \frac{nd^2}{fk}\right)$$

$$\frac{i}{i_0} = \frac{nd}{k\lambda\mathrm{V}}\,e^{-\lambda d}\left\{e^{fk\lambda\mathrm{V}/(nd)} - 1\right\} \qquad \left(0 < \mathrm{V} < \frac{nd^2}{fk}\right).$$

The symbol x has now disappeared; we retain it in future to denote $1/\mathrm{V}$. Writing also y for i/i_0 and v for nd^2/k, the equations become

$$y = f - vx\left\{1 - \frac{1}{\lambda d}(1 - e^{-\lambda d})\right\} \qquad (x < f/v) \qquad (1)$$

$$y = \frac{v}{\lambda d}\, e^{-\lambda d} x\, (e^{fd\lambda/(vx)} - 1) \qquad (x > f/v) \qquad (2)$$

As special forms of the above equations with obvious physical interpretations we have

(i) $y = f$

(ii) $y = f - vx \qquad (x < f/v)$

$y = 0 \qquad (x > f/v)$

corresponding to $\lambda = 0$ and $\lambda = \infty$ respectively.

For large values of the field, *i.e.*, for small values of x, physical considerations require that λ should be small. Under these conditions equation (1) takes the approximate form

$$y = f - \tfrac{1}{2}\,\lambda d v x\,;$$

if represented graphically the curve would have a flat portion over this range.

The critical potential for negative ions proceeding from the lower plate is given by $\mathrm{V}_0 = v/f$. In the graphic representation the two curves have for this value of V

(i) a common point $x = f/v$; $y = \dfrac{f}{\lambda d}(1 - e^{-\lambda d})$;

(ii) the same gradient, viz.,

$$\frac{1}{\lambda d}(1 - e^{-\lambda d})\left(v - \frac{f}{\lambda}\,\overline{\frac{d\lambda}{dx}}\right) - \left(v - \frac{f}{\lambda}\, e^{-\lambda d}\,\overline{\frac{d\lambda}{dx}}\right);$$

the bar indicating values to be taken at the common point. However, $\overline{d^2y/dx^2}$ calculated for curve (2) exceeds that for curve (1) by the amount $\lambda d v^2/f$. The curvature is therefore discontinuous at the critical point. This point is not therefore a true point of inflexion, but owing to the equality of gradients the two curves present the appearance of a single curve with an inflexion at the critical point. The theoretical curves exhibit thus the general characteristics of those obtained experimentally.

By applying the mathematical theory to the experimental curves we can deduce the values of λ for various pressures and applied potentials; if the values of λ thus obtained are independent of the frequency of commutation this will be strong evidence for the validity of the assumption on which the theory is based. The following procedure was adopted in the application of the theory :—

f was determined from the experimental curve and checked as described in section 2 ; v was calculated, on the assumption that the mobility (K) of the negative ion, reduced to atmospheric pressure, has the value 2·12, this value having been obtained by careful measurements at higher pressures.

For values of x less than f/v, λ was deduced graphically after writing equation (1) in the form

$$1 - e^{-d\lambda} = ds\lambda,$$

where

$$s = 1 - (f - y)/(vx).$$

For values of x greater than f/v equation (2) was expressed in the form

$$e^{-dm\lambda} - e^{-d\lambda} = dt\lambda,$$

where

$$m = 1 - \frac{f}{vx} \text{ and } t = \frac{y}{vx};$$

this form is suitable for exponential calculation.

Equation (2) was also expressed in a form adapted to logarithmic calculation. Whichever form of the equation was employed, the values of λ were determined by systematic trials.

The theoretical constants which relate to the experimental curves of fig. 4 are as follows :—

$$d = 2\text{ cm.}\ ;\ p = 59\text{ mm.}\ ;\ f_1 = 0{\cdot}5\ ;\ f_2 = 0{\cdot}53\ ;\ k = 27{\cdot}3\ ;\ n_1 = 28{\cdot}33\ ;$$
$$n_2 = 566{\cdot}6\ ;\ v_1 = 4{\cdot}15\ ;\ v_2 = 83\ ;\ f_1/v_1 = 0{\cdot}12\ ;\ f_2/v_2 = 0{\cdot}00639.$$

The corresponding graphs exhibiting the calculated values of λ plotted against $1/V$ are given in fig. 6. As it is not conceivable that λ can depend on the frequency of commutation, the assumption stated at the beginning of this section is invalid. This assumption, to which reference was made in the introductory section, has been made the basis of numerous experiments regarding the formation of negative ions.

In order to explain the experimental curves the assumption is next made that, of the electric carriers formed at the lower plate, a fraction θ consists of electrons and the remainder of negative ions. The assumption previously made is also retained, viz., that the electrons are liable to further attachment during their passage through the gas, the coefficient of attachment λ being defined as above. We will suppose that the fraction θ is a function of the

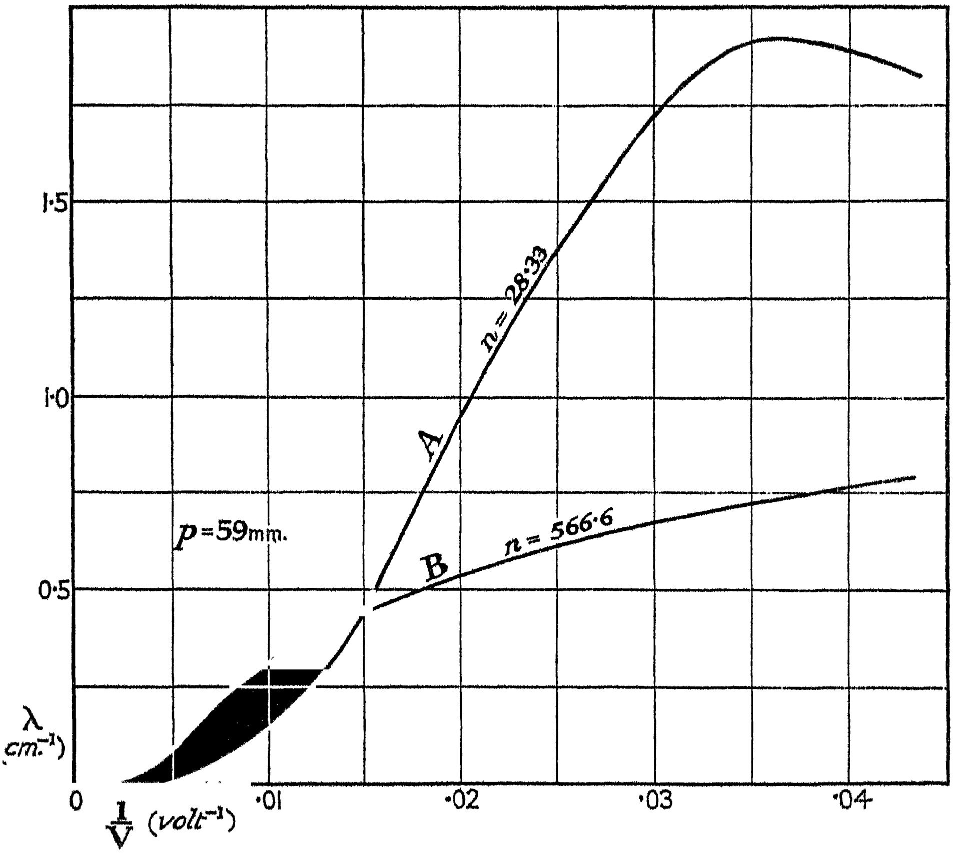

FIG. 6.

impressed voltage and of the gas pressure, also that the ions produced by the process of attachment have the same mobility as those formed at the electrode. Equations (1) and (2) take now the form

$$y = f - vx\left\{1 - \frac{\theta}{\lambda d}(1 - e^{-\lambda d})\right\} \qquad (x < f/v) \tag{3}$$

$$y = \frac{\theta v}{\lambda d} e^{-\lambda d} x \left(e^{f d \lambda/(vx)} - 1\right) \qquad (x > f/v)\,. \tag{4}$$

For the critical value of V the two curves defined by (3) and (4) have a common point

$$x = \frac{f}{v}\,; \; y = \frac{\theta f}{\lambda d}(1 - e^{-\lambda d})$$

but, in general, do not have the same gradient at this point.

We can write equation (3) in the form

$$1 - e^{-d\lambda} = ds\lambda/\theta \qquad (x < f/v) \tag{5}$$

and equation (4) in the form

$$e^{-dm\lambda} - e^{-d\lambda} = dt\lambda/\theta \qquad (x > f/v). \tag{6}$$

Equations (3) and (4) represent a curve connecting y and x when the frequency of commutation is n. Consider two such curves calculated for frequencies n_1 and n_2, n_1 being the smaller, and let the subscripts 1 and 2 refer to values corresponding to these frequencies. Suppose that $x < f_1/v_1$ over the whole range of value of x.

If $x < f_2/v_2$ it follows from (5) that $s_1 = s_2$, since λ and θ must be independent of the frequency.

Whence

$$(f_1 - y_1)/v_1 = (f_2 - y_2)/v_2. \tag{7}$$

If $x > f_2/v_2$ we deduce from (5) and (6)

$$e^{-dm_2\lambda} - \left(1 - \frac{t_2}{s_1}\right)e^{-d\lambda} - \frac{t_2}{s_1} = 0. \tag{8}$$

If the present assumption is to be valid, the experimental curves must, therefore, be such that the relation (7) is satisfied for values of x less than f_2/v_2; equation (8) will then determine the values of λ for different values of x greater than f_2/v_2. The corresponding values of θ can then be deduced from equations (5) and (6); for a physical solution they must be equivalent.

Experimental observations confirmed the validity of the relation (7). Now $\lambda = 0$ is an obvious solution of (8) which applied to (5) gives $\theta = s_1$ and to (6)

$$\theta = \frac{t_2}{1 - m_2} = \frac{y_2}{f_2} \qquad (x > f_2/v_2). \tag{9}$$

This solution cannot, therefore, be valid unless

$$\frac{t_2}{s_1} = 1 - m_2 \qquad (x > f_2/v_2) \tag{10}$$

which can be expressed also as

$$s_1 = \frac{y_2}{f_2} \qquad (x > f_2/v_2). \tag{11}$$

The validity of this relation was verified from the experimental observations.

There remains the possibility of other solutions of equation (8), which in virtue of the experimental relation (10) we can write in the form

$$z \equiv e^{-dm_2\lambda} - m_2 e^{-d\lambda} - \frac{t_2}{s_1} = 0.$$

Now $dz/d\lambda = dm_2 e^{-d\lambda}\{1 - e^{d\lambda(1-m_2)}\}$.

Since $0 < m_2 < 1$, it follows that $dz/d\lambda$ must be negative, and as z vanishes with λ no other solution is possible. This conclusion is valid as long as the experimental relation (10) or (11) is satisfied.

On putting $\lambda = 0$ equations (3) and (4) take the form

$$y = f - (1 - \theta)\,vx \qquad (x < f/v) \tag{12}$$

$$y = \theta f \qquad (x > f/v). \tag{13}$$

These equations can, of course, be obtained directly from the simple consideration that θN_0 electrons and $(1 - \theta)N_0$ ions are formed per second at the lower plate and that the electrons traverse the interval between the electrodes, in the free state.

The comparison of the theory expressed in these equations with experimental observations was effected by expressing the consequent relations (7) and (11) in the forms

$$y_1 = f_1 - \frac{f_2 - y_2}{v_2/v_1} \qquad (x < f_2/v_2)$$

$$y_1 = f_1 - \frac{v_1 x\,(f_2 - y_2)}{f_2} \qquad (x > f_2/v_2).$$

The calculated values of y_1 were then compared with the observed values.. Some of the computed values are represented by the centres of the small circles in figs. 4 and 5. The comparison was carried out for the following pressures: 7·01 mm., 20·6 mm., 40 mm., 59 mm., 92 mm., 122 mm., 182 mm.; outside this range and for moderate field-strengths the electrons or the negative ions preponderated. The agreement with the theory was sufficiently good to justify the conclusion that λ has values extremely close to zero.

For the critical value of V the two curves defined by (12) and (13) have a common point $(f/v,\ \theta f)$, but, in general, do not have the same gradient at this point. If $\overline{\theta} = 1$, they have a common gradient $f\,\overline{(d\theta/dx)}$.

6. *Conclusion.*

The physical interpretation of the foregoing theory is that the great majority of the negative ions are formed in the vicinity of the electrode at which the electrons originate; those electrons which do not give rise to negative ions near this electrode traverse in general the whole interval between the electrodes in the free state. Only an inconsiderable fraction of the ions can be formed by attachment in the body of the gas.

In the introductory section reference was made to a characteristic type of experimental curve with two components (E and I), and Loeb's explanation of these two components was given. The experimental observation that this type of curve appears only when the electrons are generated in an antechamber has been confirmed in the present experiments; the present theory leads,

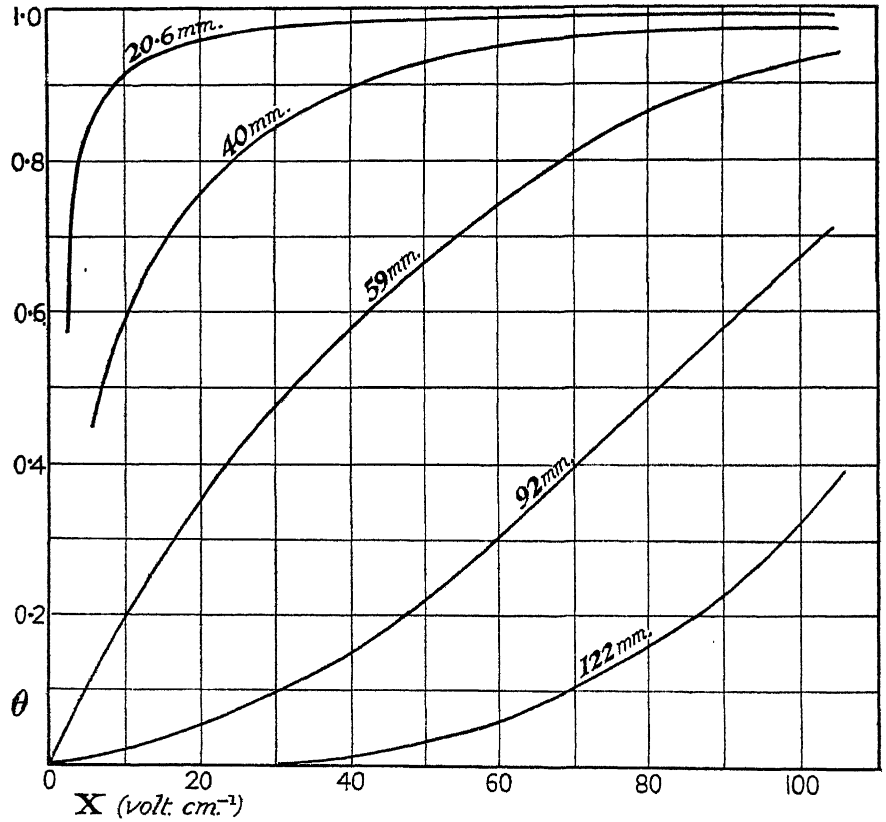

FIG. 7.

however, to an entirely different explanation. The function of the antechamber is to ensure a definite distribution of the electrons and ions which enter the measuring vessel; this distribution will depend mainly on the field conditions in the antechamber and only slightly, as a result of field penetration, on those in the measuring vessel. When, however, the electric carriers are generated in the measuring field the proportion of electrons increases with the strength of this field so that the separation of the two types of carriers is much more difficult ; the ordinary procedure of plotting current against advancing potential does not suffice to effect the resolution.

When the ionisation is produced by light the electrons issue from the plate on which the light is incident. In the previous experiments carried out by the author the ionisation was effected by alpha particles and the electrons issued from the molecules of the gas. In both cases the negative ions are formed near the electronic source.

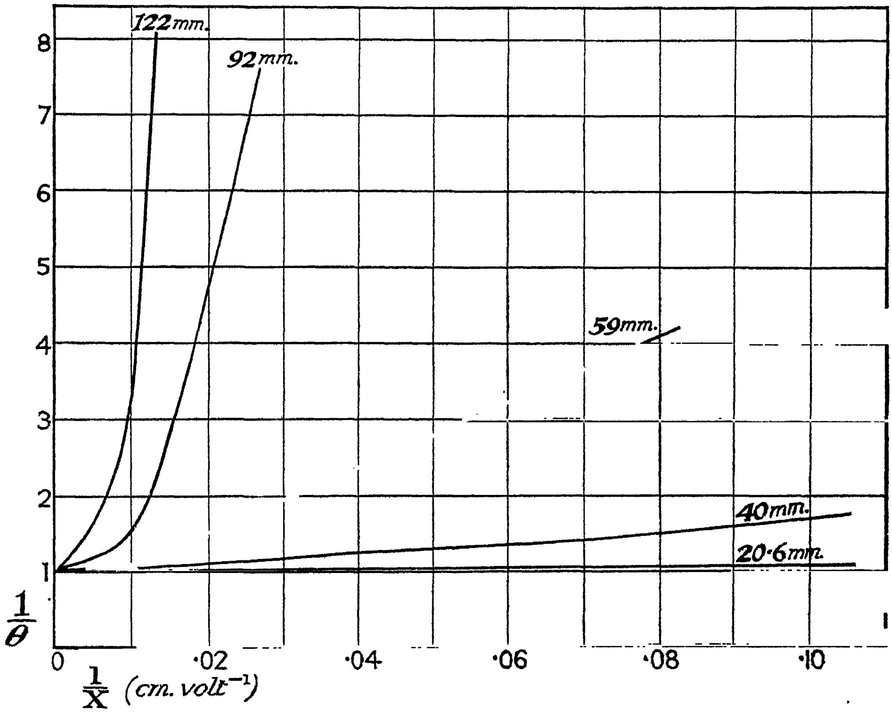

FIG. 8.

The values of θ corresponding to different field-strengths (X) and different pressures are exhibited graphically in fig. 7. On plotting the reciprocals of θ and X the family of curves exhibits the closer relation shown in fig. 8.

Summary.

The object of the investigation was to test experimentally the view that during the passage of electrons through a gas a fraction of these become attached to molecules and thus give rise to the negative ions. The electrons were generated by ultra-violet light incident upon a gold-plated electrode distant 2 cm. from a similar electrode; between these electrodes an alternating potential difference of square wave form was established. The gas contained in the measuring vessel was air at various pressures.

The experimental procedure consisted in determining for a given gas pressure and for various applied potential differences (V), the steady current (i_0) and the currents (i_1 and i_2) corresponding to frequencies of about 30 and 600 cycles per second respectively. The ratios i_1/i_0 and i_2/i_0 were then plotted against 1/V and curves of characteristic type were obtained, the range of pressures extending from 7 mm. to 1 atmosphere. These curves were then compared with curves deduced from mathematical considerations of a general character. It was found that the view-point stated above, which has been generally accepted for many years, is untenable.

The experimental curves taken in conjunction with the mathematical theory lead to the conclusion that the great majority of the negative ions are formed in the vicinity of the electrode at which the electrons originate. Those electrons which do not give rise to negative ions near this electrode traverse in general the whole interval between the electrodes in the free state.

The essential apparatus used in this investigation was acquired through a grant voted by the University of Sydney; the author desires to record his gratitude for this liberality and also to acknowledge the facilities afforded by the Staff of the Physical Laboratory.

On the Circulations Caused by the Vibration of Air in a Tube.

By E. N. da C. Andrade, Quain Professor of Physics in the University of London.

(Communicated by L. N. G. Filon, F.R.S.—Received August 11, 1931.)

[Plates 7–10.]

1. *Introduction.*

There seems a need for accurate measurements of the velocity of sound in gases, both at ordinary temperatures with chemically allied series of gases and vapours, and at high temperatures in connection with the quantum theory. The method which suggests itself at once is to utilise in some way the stationary vibrations of a gas enclosed in a tube. One procedure is to use dust to indicate the modes of vibration, in the familiar way first demonstrated by Kundt.* Two other methods which do not require the use of dust are now being tested by the writer, and will be described in due course. The successful application of any tube method demands, however, a rather more precise knowledge than has hitherto been available of the behaviour of a real gas when set into vibration in a tube of finite cross section. The present paper deals with certain features of this behaviour which do not appear to have received attention before. These are a general circulation of the air from antinode to node along the walls, returning up the centre of the tube, and a vortex motion which takes place round any obstacle, provided that the amplitude of the vibration exceeds a certain limiting intensity. The effect of this vortex motion is that the forces between two bodies placed in the vibrating gas are fundamentally different from those worked out by Koenig† on the tacit assumption of vortex-free motion.

It was observation of the behaviour of dust particles that first led to the experiments that revealed the general circulation and the vortex motion round obstacles. It is simpler, however, to discuss the nature of these air movements first and to defer the discussion of their bearing upon the formation of the dust figures described by Kundt, which are of a more varied nature than is always realised, to a second paper. Another series of investigations‡ is devoted to the explanation of the dust movements in terms of these new observations.

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* 'Ann. Physik,' vol. 127, p. 497 (1866).

† 'Ann. Physik,' vol. 42, p. 353, 549 (1891); vol. 43, p. 43 (1891).

‡ An account of which is given in 'Phil. Trans.,' A, vol. 230 (*in the press*).

The general circulation, however, cannot be left out of account in any consideration of what takes place in the tube, even if the air contains no dust particles or other obstacles.

2. *Experimental Method.*

The thermionic valve technique which has been developed of recent years offers the experimenter of to-day great advantages over those who worked on the subject in the late Lord Rayleigh's time. The gas in the tube can be maintained permanently in vibration by means of a diaphragm driven by a valve-maintained alternating current, and the phenomena studied under constant conditions which make advances easy.

The diaphragm by which the oscillations were set up in the air was that of an Amplion A.U. 7 loud speaker unit. The straight brass plate AA (fig. 1) was substituted for the original front of the unit. To this plate was soldered a wide brass tube TT into which the glass tube, usually of diameter 3·5 cm., was waxed. The diaphragm DD was, by means of a washer, gripped at the edge PP only, there being elsewhere a small clearance between it and AA. The displacement of the part of the diaphragm opposite the end of the glass tube was thus more uniform than it would be were the diaphragm gripped at the circumference of the tube. The other end of the tube was closed by a glass window, so that a beam of light could be thrown down the tube.

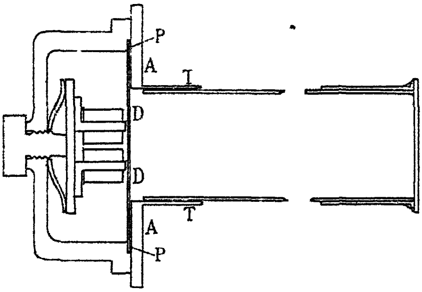

Fig. 1.

The diaphragm was driven by an oscillator of heterodyne pattern, with filter and two-stage amplifier, as shown in fig. 2. The disposition and dimensions, intended to give an approximately uniform output over a large range of frequency, are adapted from an oscillator worked out by Kirke.* This proved quite satisfactory for the bulk of the work.

To exhibit the general movement of smoke or dust in the tube a beam of light from a Leitz 10-amp. arc was thrown longitudinally down the tube, through the glass window. When desired a longitudinal cross section of the tube could be isolated by using a slit and lens. The image of the slit, illuminated by a powerful carbon arc, was thrown by means of an excellent photographic lens of focal length 50 cm. and clear aperture over 10 cm., made by Zeiss for aerial photography and kindly lent to me by Professor E. V. Appleton. A lens of this quality is not absolutely necessary, but is distinctly advantageous. The long focal length enables a beam with but feeble convergence at the focus to be used, so that the cross section is approximately constant over an appreciable length. Further details of illumination will be mentioned at the relevant places.

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* 'Experimental Wireless,' vol. 4, p. 67 (1927).

When it was desired to measure the frequency accurately the current from the oscillator was taken through a string galvanometer and the motion of the string photographed on a moving film on which a standard fork also recorded a trace. Rough measurements of frequency were made with a sonometer calibrated by standard forks.

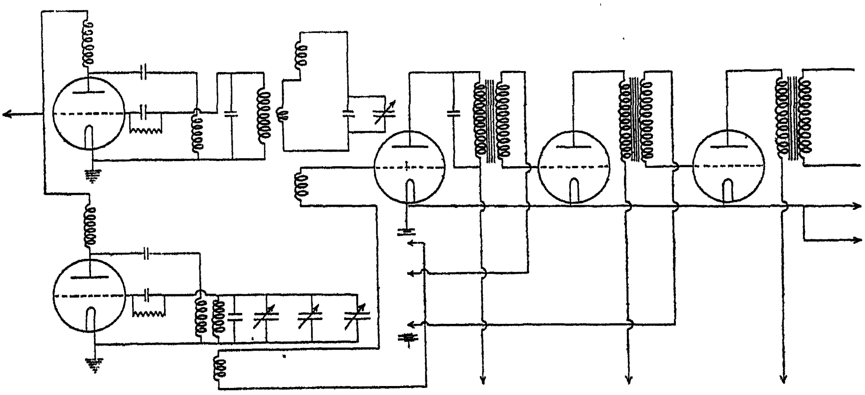

Fig. 2.

To vary the intensity of the vibration a variable resistance was arranged in parallel with the oscillator unit, whose resistance was 2000 ohms, with impedance 20,000 at a frequency 1000 ~. As a check on constancy under given conditions the current through the oscillator was measured on a milliammeter. The wave form was observed by means of a Western Electric cathode ray oscillograph with hot wire cathode and a vacuum gas tube. One pair of plates was used to indicate the difference of potential at the terminals of the oscillator unit, and the other pair was connected to the terminals of a suitable resistance (a few thousand ohms) in series with the oscillator. To enable the maximum deflection due to the potential at the unit terminals to be adjusted, a subdivided megohm was connected in parallel across the unit and a given fraction of the potential tapped off. With this arrangement a sine wave output gives an ellipse with inclined axes. The amplifier being transformer coupled, the output at higher power was, in general, distorted from sine wave form. By variation of the high tension and grid bias it was possible to produce a very good sine wave form at any particular frequency.

3. *Smoke Particles as Tracing Points.*

To investigate the motion of the air in the tube it is necessary to use some visible particle that will follow exactly the movement of the air. Smoke particles seemed likely to fulfil this condition, but, as the frequency of the vibrations excited in the air was often high, it is first necessary to show that smoke particles do behave as tracing points, the other possibility being that they move to some extent, but not fully, with the air, and thus act as obstacles over which the air washes to and fro.

The behaviour of a sphere vibrating in a viscous medium, which is the same thing as a sphere in a vibrating viscous medium, has been handled by, *e.g.*, Stokes, O. E. Meyer and Kirchhoff.[*] The resistance Z which the moving sphere experiences[†] is given by

$$Z = \frac{m}{2}\left\{\left(1 + \frac{9}{2\mathrm{KR}}\right)\frac{d\mathrm{V}}{dt} + \frac{9n}{2\mathrm{KR}}\left(1 + \frac{1}{\mathrm{KR}}\right)\mathrm{V}\right\},$$

where m is the mass of the liquid displaced by the sphere, V the velocity of the sphere, R the radius of the sphere and $\mathrm{K} = \sqrt{n/2\nu}$, n being the frequency and ν the kinematic viscosity. From this Koenig[‡] deduces the following expression for the relative motion of sphere and surrounding air

$$\frac{w_0}{v_0} = \left(\frac{1 + 3b + \frac{9}{2}b^2 + \frac{9}{2}b^3 + \frac{9}{4}b^4}{a^2 + 3ab + \frac{9}{2}b^2 + \frac{9}{2}b^3 + \frac{9}{4}b^4}\right)^{\frac{1}{2}}.$$

Here w_0/v_0 is the ratio of the maximum velocities, or of the amplitudes of motion, of the sphere and of the surrounding air, while $a = \dfrac{2\sigma + 1}{3}$ and $b = \dfrac{1}{\mathrm{R}}\sqrt{\dfrac{\nu}{\pi n}}$, σ being the ratio of the density of the material of the sphere to that of the viscous medium.

Tobacco smoke was used, the particles of which consist, apparently, mainly of water. The density of 1 was therefore assumed. The size of the particles was estimated by taking the rate of settling under gravity. The smoke was introduced into a wide, jacketed glass tube, kept at constant temperature by circulating water. After a short time a sharp top formed to the cloud, and the rate of fall of the top was then observed with a cathetometer for some 30 minutes. As a mean of four determinations, the rate of fall came out to be 0·0028 cm. per second. From this the size of the smoke particles turns out to be 5×10^{-5} cm., which compares fairly well with the only other value which I have found in the literature, namely, $2\cdot5 \times 10^{-5}$ cm.* With this value, taking $\nu = 0\cdot148$, $\sigma = 820$ and hence $a = 547$, we have the following values for the ratio of the amplitudes at different frequencies.

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[*] See, *e.g.*, Lamb's "Hydrodynamics," 4th ed., p. 635.

[†] See Basset's "Hydrodynamics," vol. 2, p. 267.

[‡] 'Ann. Physik,' vol. 42, p. 353 (1891).

Table I.

Smoke particles of radius 5×10^{-5} cm.		Cork particles of radius $1\cdot55 \times 10^{-3}$ cm.	
Frequency.	w_0/v_0.	Frequency.	w_0/v_0.
2000	0·9988	850	0·5
1200	0·99958	134	0·945
600	0·99988	120	0·955

In the table are included the results obtained for cork particles of radius $1\cdot55 \times 10^{-3}$, using the same formula and taking the density of cork as 0·24. The size given is about that of the smaller particles found in ordinary cork dust, made with a fine file.

It is clear, then, that for frequencies of 1200 and less, it is quite safe to assume that the smoke particles act as tracing points. It may be noted, however, that for supersonic frequencies this is not the case. For instance, at 300,000 ~ the ratio w_0/v_0 is 0·182 for smoke particles of the size given above, while for smoke particles of radius 1 μ the value is 0·052. Such particles are, then, practically stationary in the vibrating air when the frequencies have these extreme values, and should behave as cork particles do in an ordinary tube, a point on which experiments have been begun in my laboratory.

4. *The General Circulation between Node and Antinode.*

It is clear from what has been said that even very small cork particles in air vibrating at, say, frequencies of 100 ~ or more, do not act as tracing points but as obstacles, and work to be described has shown that each such particle ordinarily acts as a centre of vortex motion, as discussed in Section 5. The particles behave rather as initiators than as indicators of air motion. Smoke particles provide a means of investigating the true movement of the air in a dust-free tube, and accordingly experiments were carried out to observe the nature of the motion.

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* P. V. Walls and R. H. Gerke, 'J. Amer. Chem. Soc.,' vol. 41, p. 312 (1919).

Lord Rayleigh* has worked out to a first approximation the case of a viscous compressible fluid enclosed in a tube and set into vibration by a piston at one end. The terms in the second order of velocities in the fundamental equation are neglected, as usual in problems of this kind, and in addition the tube is considered, for the main problem, to be a two-dimensional one, the conditions being that the components of velocity, u and v, vanish for $y = \pm y_1$, the x axis being the direction of propagation of the wave. Certain special points are investigated for a tube of circular cross section. Rayleigh found the circulation of the type indicated in fig. 3,† the air passing from loops to nodes near the wall and in the reverse direction down the centre of the tube, the width of the direct current being $0{\cdot}423y_1$. The circulation should, of course, exist independently of the presence of particles.

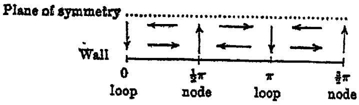

Fig. 3.

It is of interest to note that Rayleigh was led to work out this case as the result of a statement by Dvorak,‡ who made a large number of sporadic observations on the movement of particles in sounding tubes. Dvorak records that when the tube, arranged in Kundt's manner, is excited by moderately vigorous rubbing of the rod, then a cloudy wall of the silica dust used forms in each loop, of which he gives a sketch exactly reproduced in fig. 4(a). (1 shows

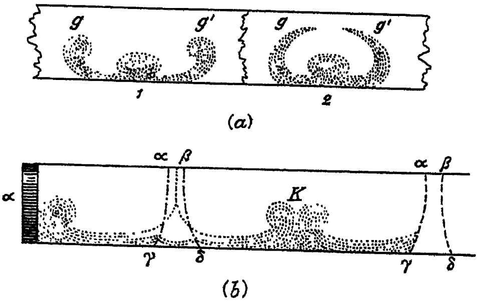

Fig. 4.

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* 'Phil. Trans.,' A, vol. 175, p. 1 (1883); 'Collected Papers,' vol. 2, p. 239 (1900).

† *Loc. cit., e.g.*, 'Collected Papers,' vol. 2, p. 256.

‡ 'Ann. Physik,' vol. 3, p. 102 (1874); vol. 7, p. 42 (1876).

the dust figure during rubbing, 2 the dust figure as the sound dies away.) He says that this is an idealised drawing, the boundaries being actually very ill-defined. If the rod is more strongly rubbed the wall becomes more marked; when the excitation has ceased it falls into two parts which move along the bottom of the tube to meet at the node, as shown in fig. 4(*b*). It is mainly on this observation that he relies for his statement that the air in the tube streams along the walls from loops to nodes, and in the reverse direction down the centre of the tube. What he was actually observing, is, however, as fig. 4 itself will demonstrate, not the circulation which he imagines, but a movement of the dust connected with the formation of the antinodal disc,* Dvorak's conditions being too unsteady, in any case, for proper formation. This is a phenomenon of complicated origin. Rayleigh apparently accepted Dvorak's statement of a true circulation without examining his experimental evidence, which is very ill-defined.

It being clear that Dvorak's observations are of little value and have, in any case, as fig. 4 shows, no reference to Rayleigh's calculations, it became of interest to see whether the circulation deduced by Rayleigh could be experimentally realised. With this object a sounding tube was carefully water-jacketed to decrease the convection, which seriously disturbs the regularity of the patterns formed, and filled with tobacco smoke from a cheap cigarette. The water jacket was in the form of a metal trough with a free surface of water through which observation was made, to avoid optical distortion as much as possible, such an arrangement being preferable, in this respect, to a cylindrical water jacket. With this arrangement the following results were obtained.

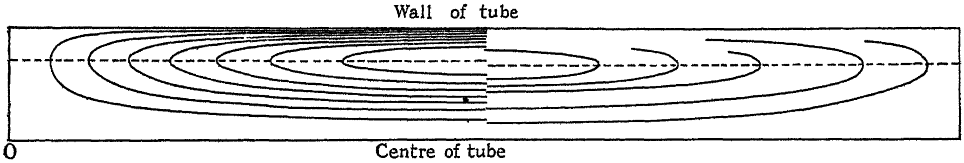

FIG. 5.

At a frequency which divides the whole tube, from diaphragm to closed end, into approximately a whole number of half-wave-lengths, a drift in the smoke rapidly develops into a regular motion of the type shown in fig. 5. The movement is from antinode to node along the wall, returning up the centre of the tube. The photographs shown in Plate 7 were obtained with flat beam illumination produced with a horizontal slit and the long focus lens already mentioned, with a larger water cell to diminish heat effects. With this cell and the water bath, disturbing convection effects were practically eliminated. The circulation is comparatively slow with the intensities obtained with our oscillator. To give an approximate idea of the relative magnitudes the motion was timed by observations of the individual smoke particles at a point near the axis of the tube and midway between node and antinode, where the lines of flow are approximately parallel and the speed is uniform. With a frequency of 600 ~ and a double-amplitude of 0·48 mm., measured by microscopic observation of individual smoke particles, as described in Section 6, the mean velocity down the centre is 0·27 cm. per second. These figures must be taken as approximate, but are probably accurate within something less than 10 per cent.

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* See 'Nature,' November 9, 1929, and also "On the Groupings and General Behaviour of Solid Particles."

Figs. 9 to 13, Plate 7, were obtained for a frequency of 600 vibrations per second. Fig. 9 shows five quarter-wave-lengths of the tube, and indicates the distinctness with which the division into segments takes place. Fig. 10 (Plate 7) shows three quarter-wave-lengths, and is a different photograph, not an enlargement from fig. 9. Fig. 11 (Plate 7) shows two quarter-wave-lengths on a third occasion. Figs. 12 and 13 (Plate 7) are photographs, obtained on different days, of a single quarter-wave-length circulation. These two figures, and one other, were used to obtain the lines of flow shown in the right-hand half of fig. 5, which receives reference later. In fig. 9 (Plate 7) the irregularity seen in the circulation at the bottom of the tube in the second segment from the right is due to a small obstacle which happened by chance to have found its way into the tube.

The circulation was detected at a variety of frequencies, dividing the tube into any number of segments from 14 down to 6. Fig. 14 (Plate 8), shows a segment from a circulation corresponding to a wave-length 91·8 cm. At the very long wave-lengths the motion is very sluggish and the lines of flow do not develop well.

As, following the initiation of the vibration, the general circulation slowly builds up, various interesting transitional forms can be observed, which have not been studied in detail. Figs. 15 and 16, Plate 8, show two such forms which are of regular occurrence.

In the early observations special efforts were made to admit the smoke in such a way as gave a streaky appearance in the tube, as it was supposed that this would be necessary for a good definition of the stream lines. It was found, however, that good stream line formation as shown, *e.g.*, in figs. 9 to 13 (Plate 7) developed from uniform smoke. This is a remarkable effect for which the

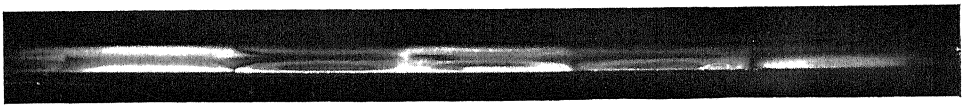

Fig. 9.—Five sections of the node-antinode circulation. Wave-length 56·5 cm.

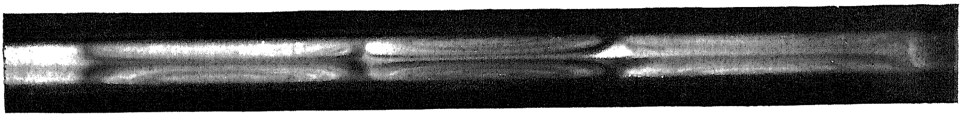

Fig. 10.—Three sections of the node-antinode circulation.

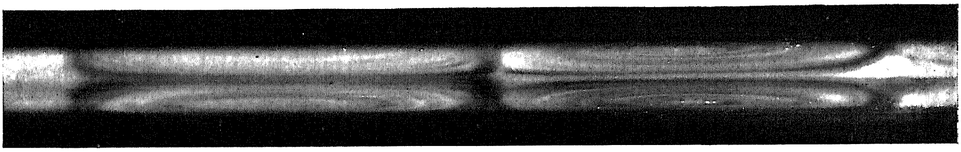

Fig. 11.—Two sections of the node-antinode circulation.

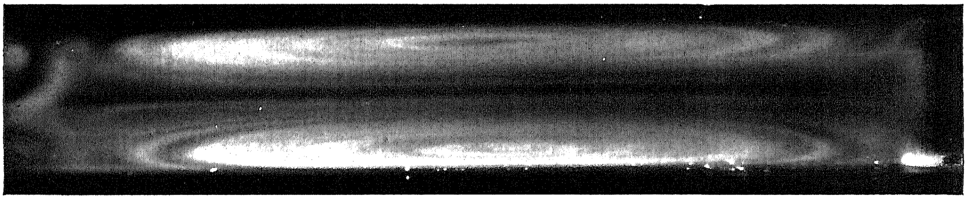

Fig. 12.—One section, node to antinode, of the circulation. Wave-length 56·5 cm.

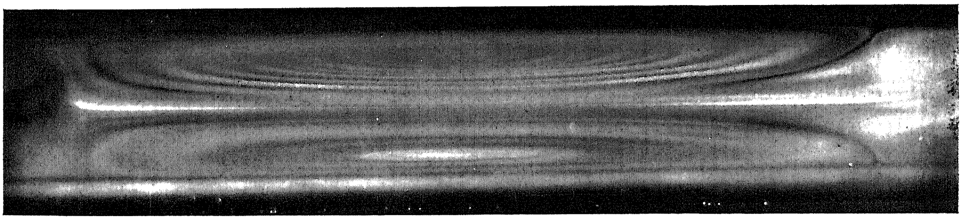

Fig. 13.—Another photograph of a node to antinode action of the circulation.

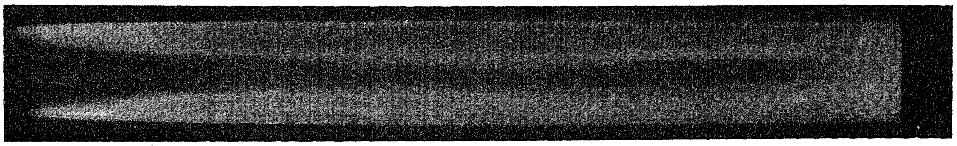

FIG. 14.—One section, node to antinode, of the circulation, with wave-length 91·8 cm.

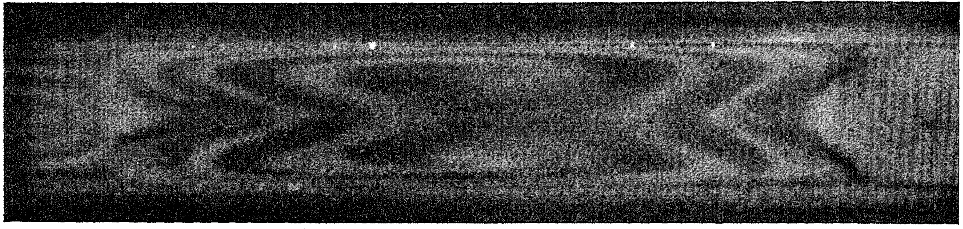

FIG. 15.—A transitional form observed during the building up of the circulation.

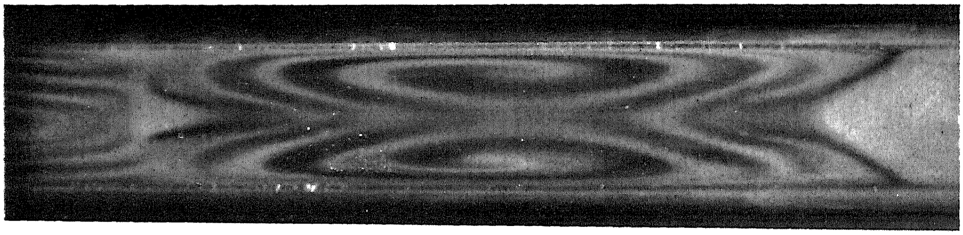

FIG. 16.—A later stage of the form shown in fig. 15.

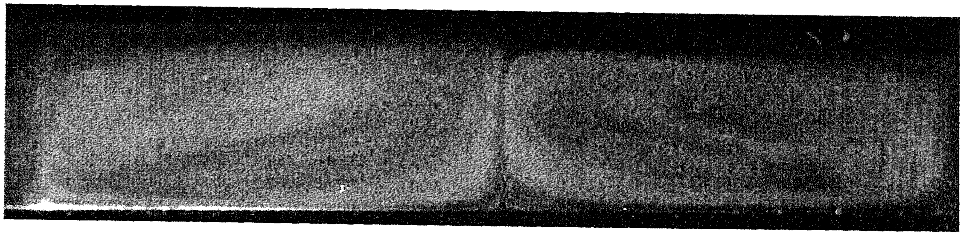

FIG. 17.—The circulation in the absence of precautions to eliminate convection: a node.

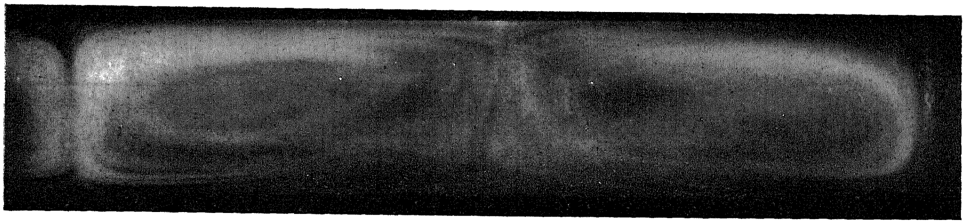

FIG. 18.—The circulation in the absence of precautions to eliminate convection: an antinode.

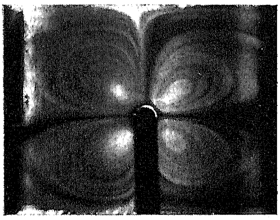

Fig. 19. — Vortex system formed by vibrating air round a cylinder, diameter 0·475 cm.

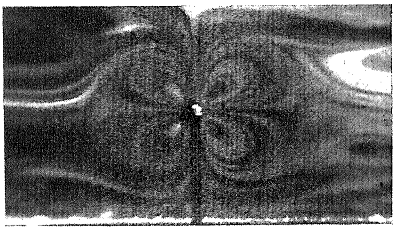

Fig. 20.—Vortex systems round cylinder, diameter 0·237 cm.

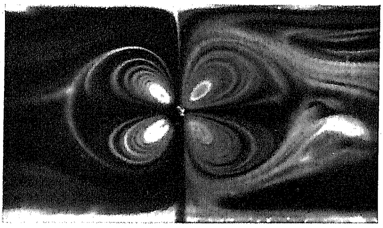

Fig. 21.—Vortex system round cylinder, diameter 0·159 cm.

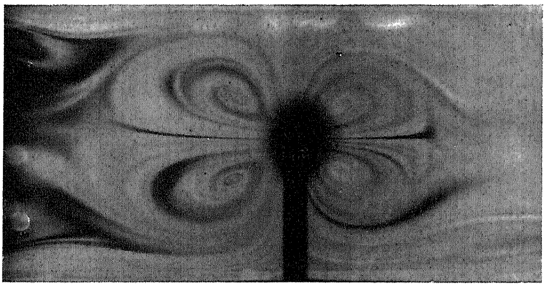

Fig. 22.

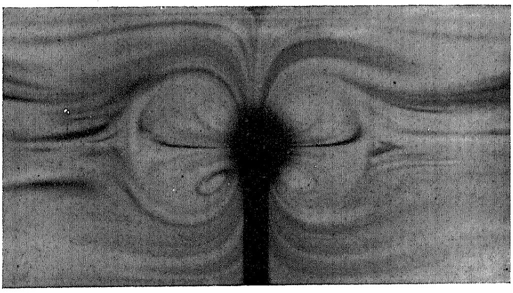

Fig. 23.

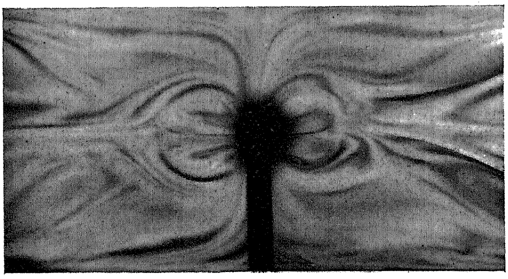

Fig. 24.

Figs. 22, 23, 24 show the effect of intensity, which diminishes in this order.

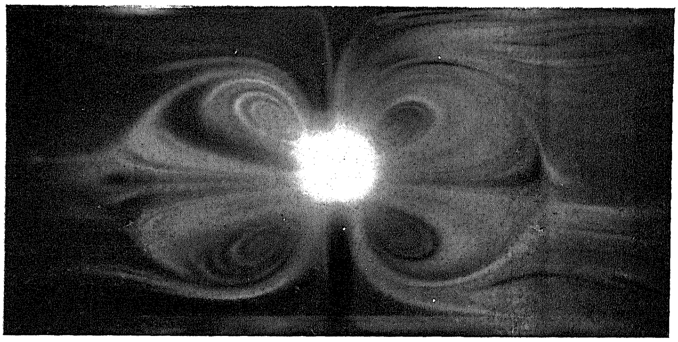

Fig. 25.—The vortex system formed round a sphere, diameter 0·317 cm.

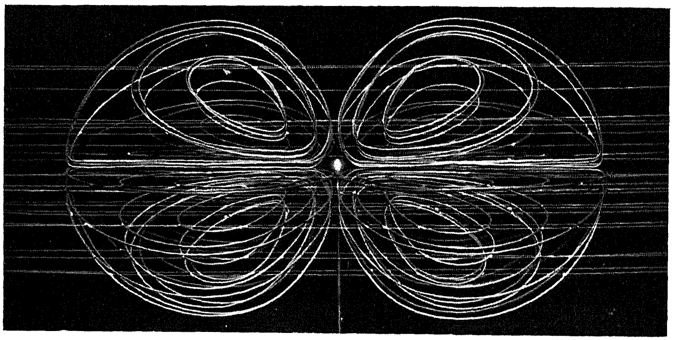

Fig. 26.—Model of the lines of flow in the vortex formed round a sphere in vibrating air.

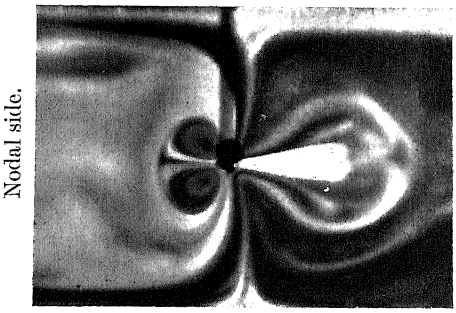

Fig. 27.—Effect of asymmetry in the intensity of the air vibrations, frequency 512.

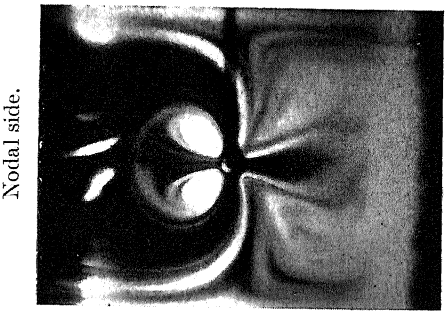

Fig. 28.—Effect of asymmetry in the intensity of the air vibrations, frequency 1024.

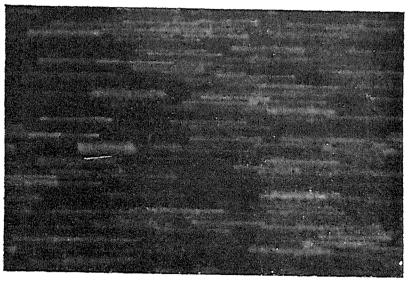

Fig. 29.—Minute cork particles in vibrating air.

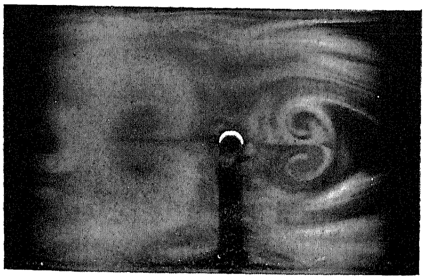

Fig. 30.—Initial stage in the development of a vortex system round a cylinder.

experimenter may be thankful. The only explanation that occurs to me is that, while the smoke particles take up the full amplitude of the air vibration within about 1 part in 10,000 at a frequency of 600, there is, nevertheless, a very small residual motion of the air past the smoke particles and this minute relative motion of air and particles will develop forces of the type calculated by Koenig (*loc. cit.*), namely attractions between particles in the direction normal to the axis of the tube, which ultimately collects the smoke into streaks, each streak initially formed collecting particles from its neighbourhood and so leaving blank spaces between streaks.

In order to obtain the true form of the stream lines it is necessary to correct for the distortion produced by refraction due to the water and the cylindrical walls of the tube. To enable this to be done a brass scale was engraved with a rectangular network, the size being such that the plane of the scale, when pushed into position, exactly coincided with the diametral plane of the tube. This was photographed under the same conditions—same water level, and the same position of the camera—as prevailed when the smoke photographs were taken, and the resulting picture enabled the true co-ordinates corresponding to any point of the original picture to be found.

From the results of these photographs the stream lines shown on the right-hand side of fig. 5 were plotted. The motion cannot be traced close to the wall of the tube, as the stream lines here are too close for the smoke to show them separately. For comparison, on the left-hand side theoretical stream lines have been plotted, using Rayleigh's formula as modified for a tube of circular cross section,

$$\psi = \mathrm{C}(r^4 - r^2\mathrm{R}^2) \sin 2kx,$$

where r is the distance from the axis of the tube, R the radius. k was chosen so as to make the wave-length equal to the same multiple of the radius as was experimentally the case. The computed values shown correspond to equal steps of ψ, these values being actually 0·25 (point of no motion), 0·21875, 0·1875, 0·15625, 0·125, 0·09375, 0·0625, 0·03125, the value 0 corresponding to the limiting case of motion as close as possible to the walls of the tube. The experimental curves are taken from well-developed stream lines, and do not necessarily correspond to equal steps of ψ. It will be seen that the general form agrees well with the computations, but that the surface at which the direction of motion changes, indicated by the dotted line, is actually farther from the wall according to experiment than the calculations indicate.

From Rayleigh's formula this distance comes out to be 0·293 R. Measurements were made on the photographs at the centre of the pattern, namely on the axial line of the smallest closed curve, since Rayleigh's approximation is most correct at this point.* They gave an average value of 0·330 R. The consistency obtained was good, different observers, reading on this point of no velocity in a given photograph, never differing by as much as 1 per cent. Measurements on the best two photographs came out as 0·333 R and 0·326 R.

It should be noted that the formula for ψ rests upon various assumptions ; terms in the second order of the velocity and of the condensation $\sigma = \log \rho - \log \rho_0$ are omitted, and it is assumed that the direct influence of friction at the walls extends through a layer whose thickness is but a small fraction of the diameter of the tube. Further, which is probably the greatest source of error, the radius of the tube is considered small as compared with the wave-length. Considering these assumptions, the agreement between theory and experiment is quite satisfactory. Recalculation of Rayleigh's results to a further degree of approximation is desirable, but promises to be an arduous task.

In the absence of precautions against convection a general circulation can be observed which clearly defines the nodes and antinodes, but the general lines of streaming are so badly distorted that it is difficult to recognise the true nature of the modified circulation. There is a strong circulation in a transverse plane which, added to the circulation in the longitudinal plane and a distortion asymmetrical about the transverse median plane, so that the effects at node and antinode are distinct in appearance, produces a very complicated motion which has been traced out, but which does not seem of sufficient interest to warrant description in detail. Fig. 17, Plate 8, shows the distorted circulation in an unjacketed tube, defining a node ; fig. 18, Plate 8, the corresponding circulation defining an antinode.

5. *Vortex Motion Round Obstacles in Vibrating Air.*

The behaviour of cork particles, described elsewhere,† led to the suspicion that they were acting as centres of disturbance of the air. Preliminary experiments were tried by fixing a single glass sphere in a tube containing smoke, and throwing the air into vibration.

These preliminary experiments indicated that vortices were formed round obstacles placed in the vibrating air, but also showed the necessity, if sharp results were to be obtained, of eliminating convection, which, owing to the heating effects of the strong illumination needed to observe the motion of the smoke, is always present unless special precautions are taken. It was also desirable to get rid of the distortion which the curved walls of the cylindrical tube introduce. An apparatus was therefore constructed on the following lines.

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* A few measurements were also made at the points where the velocity is all radial. No great importance is attached to them, as the points cannot be very accurately fixed, but within experimental error they give the same value as the measurements made on the smallest closed curve.

† 'Phil. Trans.'

A rectangular box, 16 cm. long and 3·7 × 3·7 cm. in cross section, inside measurements, was constructed of second quality optical glass about 2·5 mm. in thickness, with a lid which could be easily removed or waxed in position. This box was joined at either end to glass tubes, T, T′, of 3·5 cm. internal diameter, and to lead smoothly from the tube to the box, without discontinuities of surface liable to produce vortices, brass pieces with surfaces of continuous curvature leading from a circular to a rectangular cross section were inserted as shown in fig. 6. The lid of the box was pierced with a hole which enabled either a cylindrical rod to be inserted, as shown in fig. 6, or a suspension apparatus, described in the forthcoming paper on dust figures, to be adopted.

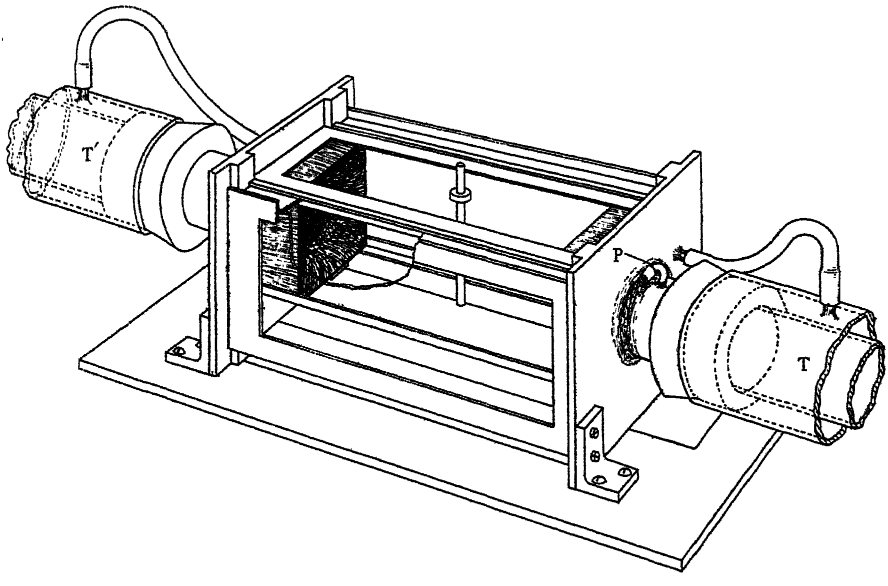

Fig. 6.

The glass box was enclosed in a second glass box, the sides of which were mounted in a metal framework, enabling a circulation of water to bathe the two sides and the bottom of the box. The glass tubes T and T′ were likewise water-jacketed. The whole tube so made was closed at one end by a movable brass disc, attached to a glass tube fitting closely inside the tube T. An air-tight joint was made from the tube T to this sliding tube by means of a rubber sleeve. A similar sliding tube, open at one end and carrying at the far end the oscillator unit, protruded into T and was likewise made tight with a rubber sleeve. By means of this arrangement not only could the tube length be varied to bring it into resonance with any given frequency, but a node or anti-node of the motion could be made to fall at any desired part of the glass box. A small tube P, and one on the other side of the box, which does not show in the diagram, were provided to introduce the smoke.

It is generally desirable to illuminate the box with a flat beam of approximately uniform rectangular section, say about 5 or 6 cm. wide and a few millimetres thick. This enables observations to be made on the motion in any given plane, uncomplicated by motion in adjacent or intervening parts of the air. The slit and long-focus lens mentioned in Section 2 were used. The slit could be turned to any desired azimuth, while a mirror under the box, arranged to turn about an axis parallel to that of the tube and in general fixed at 45°, enabled a vertical beam instead of a horizontal beam to be used when desired. In this way any desired section of the motion could be isolated.

The first experiments were carried out with cylindrical obstacles, to get a two-dimensional simplicity. Rods of silver steel were used. The smoke used was again tobacco smoke from a common cigarette, which, among a large number of smokes tried, was found to be the most convenient and regular in results, and to produce the smallest particles. The smoke was blown from the mouth, through a long calcium chloride drying tube, into the box. The oscillator was set in motion at a given frequency, and the sliding tubes in T and T′ adjusted until the obstacle was at an antinode.

When the intensity is suitable, a point to be discussed shortly, a vortex motion with four loops, as shown, *e.g.*, in fig. 19, Plate 9,* is formed round the cylinder. The direction of the circulation is as indicated in fig. 7. This effect was obtained with cylinders of diameters ranging from 0·2 to 0·6 cm., and also with wires of diameter as small as 0·0081 cm., as described in the forthcoming paper on dust figures. Spherical obstacles, namely, steel balls made for bearings, were also used. Fig. 25, Plate 10, shows a median section through the vortex system formed round a sphere of diameter 0·317 cm. The general appearance is the same, but the shape of the lines of flow is modified. A representation of the complete vortex system can be obtained by rotating the lines of flow shown in the picture about an axis through the centre of the sphere and parallel to the vibration vector; what are cross sections of four cylindrical vortices in the cylindrical case shown, *e.g.*, in fig. 21, Plate 9, are cross sections of two toroidal vortices in the spherical case represented in fig. 25, Plate 10. A wire model of the lines of flow round a sphere was constructed from photographs, and is shown in fig. 26, Plate 10. The upper quarter, facing the spectator, of the complete system is shown removed, to enable the circulation to be better seen. For observation with both the cylinder and the sphere a vertical beam was sometimes used, and served to confirm the general appearance here described.

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* In all these photographs of vortex systems about obstacles the black band seen extending from the obstacle across the tube is not a material bar, but the shadow of the obstacle, which is illuminated from the side corresponding to the top of the pictures.

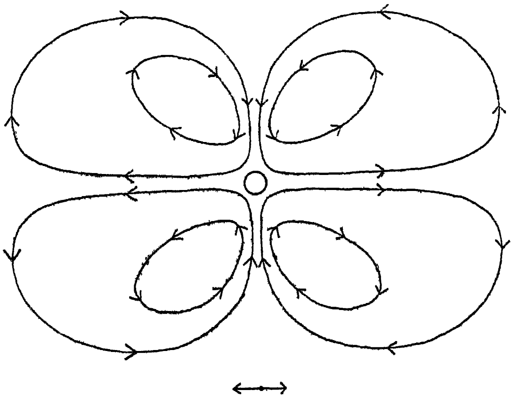

FIG. 7.

The size of the rod has an effect on the size of the vortex system. The photographs shown in figs. 19, 20 and 21, Plate 9, represent respectively the systems obtained with rods 0·475, 0·237 and 0·159 cm. in diameter. The intensity of the vibration was kept as nearly as possible the same in the three cases.

To investigate the effect of changes of intensity a variable resistance was put in series with the diaphragm unit, by which the amplitude of the diaphragm could be controlled. With large intensities the general circulation discussed in Section 4 is very strong, and the air round the obstacle is streaming so vigorously in this circulation that the vortex can never form properly, although there are signs of its inception. As the intensity is lowered the general circulation weakens relatively to the vortex motion, till a stage is reached where the vortex is large and well formed, as shown in fig. 22 (Plate 9). A further lowering of intensity leads to a decrease in the size of the vortex system, which is still well-formed, as shown in fig. 23 (Plate 9). With further decrease of intensity the movement of the air within the vortex becomes sluggish, and the vortex is not only small but also tends to be irregular in shape, with an ill-defined inner circulation, as shown in fig. 24 (Plate 9). Finally, with very low intensity no vortex at all can be detected. The conditions that attend the initiation of vortex motion are discussed in Section 7.

These experiments on the effect of intensity were carried out with a rod of diameter 0·237 cm. and a frequency of 512, the length of the tube being adapted so that this was a resonant frequency. The cylinder throughout was at an antinode, so that the amplitude of the vibration is uniform in its neighbourhood, unless otherwise specified. Experiments were also carried out on the effect of changing the frequency to either side of the resonant frequency. The effect of such changes is, of course, to reduce the intensity of the vibration, and it was found that progressive diminution or increase of frequency had the same effect as the diminution in intensity brought about by changing the amplitude of the diaphragm. That is, at large intensities, however brought about, the general circulation between node and antinode is the predominating factor, the vortex systems round the particles being ill-formed or suppressed; at medium intensities the vortex systems are strong and well-formed; at low intensities they are very feeble. This effect is important in connection with the behaviour of dust particles in the tube.

When the frequency is varied, the cylinder being always at a fixed distance from the closed end of the tube, the cylinder does not, of course, remain exactly at an antinode, but the departure is small. For example, the resonant frequency being 512, a range of frequency 495–530 was employed. The cylinder was 49·8 cm. from the closed end of the tube. At the extreme frequencies the cylinder is only 1·7 cm. and 1·8 cm. from the antinode when the distance from node to node is, respectively, 32·1 and 34·4 cm. These positions are so near the maximum that the intensity does not vary markedly in the neighbourhood of the obstacle.

Experiments were carried out to observe the effect of an asymmetric distribution of amplitude in the neighbourhood of the obstacle, by displacing the cylinder from the antinodal position. Fig. 27, Plate 10, represents the motion with frequency 512, and with the rod at a distance of 11 cm. from the antinode, which means 5·6 cm. from the node. At this position the corresponding variation of amplitude, expressed in percentage change per centimetre, is 16 per cent. The vortex system is well-formed on the antinodal side, but on the nodal side the two cylindrical vortices seem to be forced away from the axis of the tube, while the air streams through the centre towards the node, the motion becoming dissipated at some little distance from the cylindrical obstacles. The circulation is feeble in the vortices on the nodal side. Fig. 28, Plate 10, shows a similar state of affairs with a frequency 1024 and the obstacle 5·8 cm. from the antinode, *i.e.*, 2·5 cm. from the node. The amplitude is here varying by 37 per cent. per centimetre, and the appearance is remarkable. The position of the node is on the extreme left of the photograph.

6. *The Measurement of Amplitude.*

Since smoke particles take up the full amplitude of the motion of the air at the frequencies with which we are concerned, they can be used to measure the amplitude if suitable illumination and a suitable method of observation are used. The water-jacketed glass box of fig. 6 contained the smoke under observation. The axis of the illuminating beam and of the observing instrument were at right angles to one another, as in ultra-microscopic work, the observation being horizontal. The source of light was a 12-volt lamp with a line-coil filament taking 6 or 7 amperes, fixed at about 1 metre above the top of the glass box. By means of a photographic lens of working aperture 2·9 and focal length 4 inches, a diminished image of the filament was formed at the spot where the amplitude was to be measured, stray light being shielded by a tube of black paper and a suitable black paper screen. A thick water cell containing ammoniated copper sulphate was inserted in the path of the beam. For observation a reading microscope with a vertical and horizontal travel was used; the objective was a Beck 40-mm. apochromatic, N.A. 0·16, which is very light-strong, and the eyepiece a × 9·6. In conjunction with this eyepiece a Swift thread micrometer was used, of the type in which a travelling thread is moved by a divided head so as to be always parallel to a fixed thread running diametrically across the field. With the arrangement specified, 535 divisions of the micrometer head were equivalent to 1 mm.

The smoke particles show as bright points on a dark ground. When the air is thrown into vibration they appear as short bright lines terminating in minute discs, these enlargements being, of course, the effect of the particle being instantaneously at rest at the extremes of its librations. Attempts to photograph the smoke particles in motion were not successful, but a good idea of the appearance can be obtained from fig. 29, Plate 10, which is a picture of minute cork particles (approximate diameter 0·002 cm. and greater) in vibrating air. The difference of length shown by the traces is due to the variation of size among the particles present, the smallest particles giving, of course, the longest traces.

It is not possible to eliminate altogether the general drift of the particles across the field. This has its origin partly in convection, partly in the general circulation described in Section 4. The convection effect is rendered very small by the water-jacketing of the box and the water cell in the path of the illuminating beam, the illumination being switched on only just when readings are being taken. The general circulation cannot be avoided, but at the lower intensities it is not sufficient to cause grave difficulty. By traversing the cross section of the box a place could be found where the drift was a minimum. The wires of the micrometer were set roughly at the correct distance apart, and observation was made, while the particles drifted obliquely across the wires, as to whether the distance was too small or too great. It was then corrected and further observations made. No attempt was made to adjust the distance between the wires at the moment when observations were being made, as this method was found to be unsatisfactory. Only the particles sharply in focus were used for observation. Every amplitude measurement used was the mean of 10 independent observations.

Extensive measurements of the amplitude (or rather the double amplitude, since that is what is directly given by the length of the trace) which conclusively prove the feasibility of the method were made in connection with the experiments on the initiation of vortex motion described in Section 7. This method of measuring amplitude makes it possible to measure the energy of the sound vibration in the column of air, and so provides us with a source of sound of known absolute energy. An open tube can be used, and the amplitude measured at the antinodes. It is difficult to measure the amplitude at the open end itself, owing to disturbances in the mouth of the tube. A fuller description of the method will appear in due course.

7. *The Initiation of Vortex Motion.*

It being established that under certain conditions vortex motion is generated round an obstacle by air oscillations, it is of interest to examine the critical conditions for vortex and for vortex-free motion. The principle of dynamical similarity tells us what combination of the conditioning factors—frequency, amplitude, kinematic viscosity of the medium and linear dimensions of the obstacle—are involved. For the motion to be similar in two cases the slope of the lines of flow at similarly situated points must be the same with respect to the direction of the vibration vector. This slope, which is dimensionless, must be a function of the velocity v, the acceleration $\dot{v}$, the kinematic viscosity ν, and the diameter, or other linear dimension, d of the obstacle. We can see at once that the density cannot occur, since M is not elsewhere involved in the equation.

Let the slope = some function of $v^x \dot{v}^y d^z \nu^u$. Equating the indices of L and T to be equal to zero, we have,

$$x + y + z + 2u = 0$$

$$x + 2y + u = 0,$$

which gives

$$v^{-3u-2z} \dot{v}^{u+z} d^z \nu^u \text{ dimensionless}$$

or

$$f\left(\frac{\dot{v}\nu}{v^3}, \frac{\dot{v}d}{v^2}\right) = 0$$

which may be written

$$\frac{\dot{v}\nu}{v^3} = g\left(\frac{\dot{v}d}{v^2}\right).$$

In the case of a periodic simple harmonic motion $y = a \sin nt$

$$\dot{v} = n^2 a$$

$$v = na$$

dimensionally, from which we get

$$\frac{a}{d} = \psi\left(\frac{na^2}{\nu}\right).$$

The conditions for initiation of vortex motion are therefore represented by finding experimentally a_c/d as a function of $n_c a_c/\nu$ where a_c and n_c are the critical amplitude and frequency for which vortex motion just begins with a given diameter d of the obstacle. It was found, with either a sphere or cylinder in the channel, that when, with a given frequency, the amplitude was steadily increased from a very small value, a stage could be detected for which vortex motion just began. The characteristic appearance is the sudden jet of air, in the case of the cylinder in the diametral plane, in the case of the sphere in the diametral line parallel to the vibration vector, which shoots out from the centre of the obstacle on either side when the air is set into vibration. This jet is the first stage in the development of the vortex; on either side the flow of the air so thrown out diverges and builds up two loops of the complete vortex system. The small vortices which are formed when the amplitude, at a given frequency, is just sufficient to produce vortex motion, can often be clearly distinguished, but when, as happens, the smoke is not suitably disposed, in filaments, to show the feeble circulation, the initial motion just described can always be seen. That the criterion is reliable is strongly suggested by the regularity of the observations based upon it.

The process described above, which constitutes the first step in the development of vortex motion, is illustrated in fig. 30, Plate 10, which was obtained with a rod 0·318 cm. in diameter, and a frequency of 512 ~, just after switching on the sound. The intensity was large, and the vortex system would eventually build up into something of the kind illustrated in fig. 19, Plate 9, were it not that with the intensity used the node to antinode circulation, which takes some time to establish itself, would overwhelm it.

The quantitative observations were made with spheres of five different diameters, 0·237, 0·318, 0·475, 0·560 and 0·633 cm. respectively. The hardened steel balls made for ball bearings, which are extremely true, were used. To mount a sphere it was softened and drilled to take a fine wire 0·8 mm. in diameter, which in its turn was attached to a thin plate of iron. The plate was waxed to the bottom of the glass box in which it extended from side to side, while the two edges normal to the vibration vector were carefully sloped away so that no sharp edges were presented which might cause vortices. The sphere was arranged so that its centre came at the middle of the box. A flat horizontal beam of light was used for illumination, and observation was made both by looking obliquely down on the diametral plane so illuminated, and by the use of a mirror arranged so as to give a vertical view.

A given frequency is chosen, and the tube adjusted so as to make the sphere, placed in the middle of the box, be at an antinode. The amplitude is altered by means of variable resistances shunted across the loud speaker unit. Starting with large amplitude well-formed vortex motion occurs whenever the vibration is started. The shunting resistance is gradually diminished until, when the vibration is initiated, the characteristic appearance of vortex motion already described can just be seen. The method of diminishing amplitude was found to be more reliable than that of increasing the amplitude and looking for the first sign of vortex motion, which, of course, is another possible method of procedure.

The measurements of amplitude were made by microscopic observation of the smoke particles, as described in Section 6. At the low intensities which are in question when the initiation of vortex motion is concerned, the general circulation is either non-existent or very feeble, so that the drift of particles in the water-jacketed chamber is very slow. The mean of the values taken by two different observers usually agreed to within considerably less than 5 per cent.

The finite size of the box may possibly have a secondary influence on the critical conditions. To find accurately the values for an infinite channel would necessitate the use of two or three channels of different sizes, and would require a very extensive set of amplitude readings, to give the high precision necessary. As it was only desired to get a general view of the law governing the critical conditions, and an approximate value of the constants involved, no attempt was made to estimate the influence of the walls of the box. The regularity of the results obtained with spheres of different sizes shows that, in any case, this influence cannot be very large. The results are given in the following table, ν, the kinematic viscosity of the air, being taken as 0·150 c.g.s. units, while d is the diameter of the sphere, f the frequency of the vibration $y = a \sin nt$, a the amplitude of the air vibration.

Table II.

d.	f.	n.	a.	na^2/ν.	a/d.	$\sqrt{2\nu/n}$.	$\sqrt{(2\nu/n)}/d$.
cm.	~		cm.				
0·237	780	4900	0·0034	0·377	0·0143	$7{\cdot}82 \times 10^{-3}$	0·033
0·237	512	3217	0·0051	0·557	0·0215	9·65	0·042
0·237	420	2639	0·00685	0·817	0·0289	10·6	0·045
0·318	840	5275	0·00112	0·044	0·0035	7·54	0·024
0·475	312	1960	0·0050	0·325	0·0105	12·4	0·026
0·475	512	3217	0·00145	0·045	0·00305	9·65	0·020
0·56	120	754	0·00985	0·488	0·0174	19·9	0·035
0·632	89	559	0·0115	0·493	0·0182	23·2	0·037
0·632	220	1382	0·00300	0·083	0·0047	14·7	0·032

Fig. 8 shows a/d plotted against na^2/ν. It will be seen that the values obtained with the five different spheres, indicated on the diagram by five different symbols, give approximately a straight line, there being no evidence that the size of the sphere, within the range $d = 0{\cdot}237$ to $d = 0{\cdot}632$ cm., produces any systematic deviation. The two bad points are for different sized spheres, and the five points that lie well on the line represent three different sized spheres. The readings corresponding to the two bad points were made, in each case, at the end of the day when the observers were not fresh, which probably leads to inaccurate values for the amplitudes, but all the measurements made have been given lest there should be any prejudice in the matter of selection. Points below the line represent conditions for vortex motion, points above for vortex-free motion.

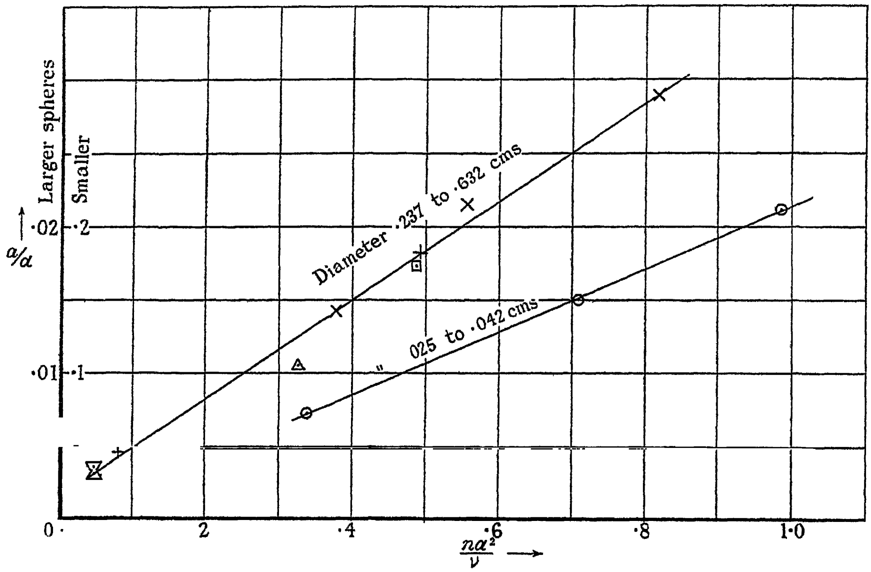

FIG. 8.

The equation representing the straight line is

$$\frac{a}{d} = 0\cdot0017 + 0\cdot0331\,\frac{na^2}{\nu}$$

which, it will be observed, does not go through the origin. If the straight line really represents the nature of the law outside the limited region of values of a/d for which the experimental points were obtained, we can deduce results for conditions represented by $na^2/\nu = 0$ and $na^2/\nu = \infty$, which have a physical meaning, although no great significance can, perhaps, be attached to such wide extrapolation. For $na^2/\nu = 0$ the value of a/d is $0\cdot0017$ or $d = 600a$, which can be interpreted to mean that when n becomes very large and a very small, na, the maximum velocity, remaining finite, the condition for vortex motion is that the diameter of the sphere must exceed 600 times the small amplitude. At the other limit, when n tends to 0, a to ∞, na remaining finite, we have the case of a steady non-periodic motion, from which we can find the Reynold's number in the case of uniform flow past a sphere. The result is that $v_c d/\nu = 30$, where v_c is the critical velocity which just causes vortex motion behind a sphere. This value may be compared with the measurements of the critical velocity for the case of steady flow past a sphere made by Nisi and Porter.*

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* 'Phil. Mag.,' vol. 46, p. 754 (1923).

According to their formula, which allows for the influence of the finite channel, the values of $v_c d/\nu$ should be 9·1, 11 and 12·4 respectively for spheres of diameter 0·237, 0·475 and 0·632. These are of the same order as the value 30 found by extrapolation.

While these results for spheres whose diameters are a few millimetres are consistent and satisfactory, there appear to be difficulties in the way of supposing that the constants thus obtained would be valid for very small diameters. For one thing, the above constants indicate that with a frequency of 840 ~, diameter of 0·0081 cm. and a double-amplitude of 0·0073 cm. (which gives $na^2/\nu = 0 \cdot 47$ and $a/d = 0 \cdot 45$) there should be no vortex motion, the curve of fig. 8A showing 0·01 as the critical value of a/d when $na^2/\nu = 0 \cdot 47$. Yet experiments carried out with a wire of diameter 0·0081 cm., in connection with the dust experiments described elsewhere,* showed that with this diameter, frequency and amplitude, very well marked vortices were formed. It is true that a cylinder was being used, instead of a sphere, in these experiments, but the discrepancy is too large to be accounted for in this way. Now cases are already known in which the constant determining vortex motion, obtained from the principles of dynamical similarity, is greater for small objects than for large ones. E. G. Richardson, for instance, studying the Aeolian tones, found that the value of v/nd (where v is the velocity of the wire, d its diameter and n the frequency of the tone) while constant for values of d from 1·15 to 0·41 cm., increased by over 50 per cent. when the diameter decreased to 0·1 mm.† For edge tones he has recently found a similar effect.‡ In the case of a steady motion it is well known that the constant which holds for a small sphere obeying Stokes' law cannot be applied to larger spheres. As, in considering the results of the experiments of previous workers, it was desired to have some guide as to whether vortex motion had set in or not, one or two orienting experiments were carried out with small obstacles.

The ends of fine gold wires, 0·0081 cm. in diameter, were just fused in a Bunsen flame, by which simple process very small spheres can be prepared. The sphere can then be easily mounted in the channel by means of the wire to which it is attached. The following results were obtained for the initiation of vortex motion.

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* 'Phil. Trans.,' A, vol. 230 (*in the press*).

† 'Proc. Phys. Soc.,' vol. 36, p. 153 (1924).

‡ 'Proc. Phys. Soc.,' vol. 43, p. 394 (1931).

Table III.

d.	f.	n.	a.	na^2/ν.	a/d.	$\sqrt{2\nu/n}$.	$\sqrt{(2\nu/n)}/d$.
cm.	~		cm.				
0·0416	840	5280	0·0031	0·338	0·074	$7{\cdot}53\times10^{-3}$	0·181
0·0251	840	5280	0·0053	0·988	0·211	7·53	0·300
0·0251	1200	7540	0·00375	0·707	0·150	6·30	0·251

The results for the small spheres are indicated by the circles in fig. 8. They lie on a straight line which passes through the origin, signifying that

$$\frac{na^2}{\nu}\Big/\frac{a}{d}=\frac{nad}{\nu}=\frac{v_c d}{\nu}$$

is constant, where v_c is the maximum velocity of the pulsating air a long way from the obstacle in the critical case. It therefore seems of interest to plot $v_c d/\nu$ against a/d, or, to compress the scale, against log a/d. Fig. 9 shows the results treated in this way, the curve to the left representing the results with the range of larger spheres, and the horizontal straight line to the right that for the smaller spheres. Over a certain range of a/d for the larger spheres, and over the whole experimental range of a/d for the smaller spheres $v_c d/\nu$ approximates to a constant value, showing that within the ranges in question a fixed value of $v_c d/\nu$ leads to similar vortex systems. However, for small values of a/d there is a falling off of the values of $v_c d/\nu$, as shown in the figure.

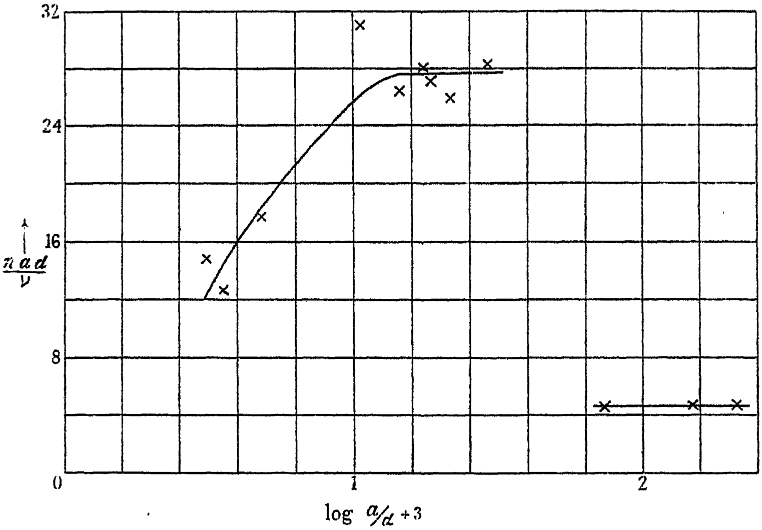

Fig. 9.

The constant value of $v_c d/\nu$ for the larger spheres differs markedly from that for the smaller spheres, as is obvious from what has already been said.

We may now consider in a general way the possible cause of the vortex systems. Lord Rayleigh's mathematical discussion of the general circulation described in Section 4 is represented physically by a layer of air adjoining the solid boundary within which the effects of the tangential forces due to viscosity are appreciable, and by irrotational oscillation outside this layer. The thickness of the layer, whose influence is represented in the solution by an exponential term in $e^{-\beta y}$, may be taken as measured by $1/\beta = \sqrt{2\nu/n}$. Lord Rayleigh shows in the three cases discussed* that the effect of a boundary layer is to produce a steady vortex flow, proceeding, in the neighbourhood of the solid surface, from the node, or region where the oscillations are greatest, to the antinode, or region where the oscillations vanish. These results suggest that in the case of the sphere the main features of the flow may be an irrotational oscillation imposed on a steady vortex motion and that the vortex flow near the sphere should be from a diametral plane normal to the vibration vector, where the oscillation is most vigorous, to the diameter parallel to the vibration vector. This is what is actually observed. Discussion of the forces between two spheres due to the type of flow adumbrated is postponed until the completion of some experimental work on the subject now being carried out in my laboratory.

The thickness of the layer of viscous effect, as measured by $1/\beta = \sqrt{2\nu/n}$, is given in Tables II and III, as is also the ratio of this thickness to the diameter of the obstacle (last column). It will be seen that whereas this ratio has values lying within the comparatively restricted range 0·020 to 0·045 for the larger spheres, for the smaller spheres the ratio is much larger, varying from 0·181 to 0·300. This goes far to make the difference of the constants for larger and smaller spheres understandable.

Koenig's theory of the formation of dust ridges† has led to various experiments being carried out on the forces between two spheres in a vibrating medium both with the line joining the centres normal to the vibration vector, and with it parallel to the vibration vector. The calculations of this theory are based on the assumption of a vortex-free motion. The most extensive series of observations are those of Koenig's student, Georg Thomas,‡ adduced by

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* *Loc. cit.*

† W. Koenig, 'Ann. Physik,' vol. 42, pp. 353, 549 (1891); vol. 43, p. 43 (1891).

‡ G. Thomas, 'Ann. Physik,' (4), vol. 42, p. 1079 (1913); W. Koenig, 'Phys. Z.,' vol. 12, p. 991 (1911).

Koenig in support of his theory. Following W. Zernov,[*] Thomas used a small box fastened to the prong of a tuning fork—the wave-length produced by which was large compared to the size of the box—to move a body of air as a whole with simple harmonic motion, and investigated the forces between two spheres immersed in the moving air. He used two frequencies, 81 and 61, and two amplitudes, 0·1 cm. and 0·075 cm. In the following table are set out the values of na^2/ν and a/d which have been computed from his figures.

Table IV.

d.	f.	n.	a.	na^2/ν.	a/d.
cm.	~		cm.		
1·56	81	509	0·1	33·8	0·064
1·04	81	509	0·1	33·8	0·096
0·56	81	509	0·1	33·8	0·179
1·56	61	383	0·075	14·4	0·048
1·04	61	383	0·075	14·4	0·072
0·56	61	383	0·075	14·4	0·134

Comparison with fig. 8 shows that in all cases there must have been vortex motion in Thomas's experiments, and reference to his results shows that, in fact, in no instance did he get perfect agreement with Koenig's theory. The best agreement was with the experiment last recorded in the above table, which has the largest value of a/d for the smaller value of na^2/ν, that is, the experiment for which the approach to the conditions for vortex-free motion is closest. Of our experiments the one closest to Thomas's actual magnitudes concerned a sphere of diameter 0·56 cm. in air vibrating with a frequency 120 and an amplitude 0·075 cm. The result is not conclusive, as the frequency is higher than Thomas's, but well-marked vortex motion was, in fact, obtained under these conditions.

S. Cook,[†] working with spheres of glass and of wax, having diameters 0·02 to 0·03 cm., obtained results which contradicted Koenig's theory, and so came into conflict with the deductions of Thomas's experiments. In particular he used for his chief experiment a frequency of 1287 and an amplitude which he estimated at 0·02 cm. For 0·02 cm. diameter we have from these figures $na^2/\nu = 21 \cdot 6$, $a/d = 1$. According to our experiments with the small gold spheres, described above, the limiting value of a/d is 4·2 for $na^2/\nu = 21 \cdot 6$, which shows that vigorous vortex motion round the obstacle should take place under Cook's conditions. This was confirmed by direct experiments with a gold sphere 0·025 cm. in diameter, a frequency of 1200 and an amplitude, measured by the smoke particles, of 0·02 cm. Vigorous vortex motion was observed.

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[*] W. Zernov, 'Ann. Physik,' vol. 26, p. 79 (1908).

[†] 'Phil. Mag.,' vol. 3, p. 471 (1902).

It is clear, then, that not much importance can be attached to previous attempts to verify Koenig's theory with small spheres, as the conditions of vortex-free motion which lie at the basis of the theory did not prevail in any experiment. The quantitative laws of repulsion between cylinders and spheres surrounded by the type of vortex motion here discussed are being investigated experimentally in my laboratory.

An isolated experiment was carried out to compare the critical conditions for a sphere and a cylinder of the same diameter, namely, 0·237 cm., and at the same frequency, 512. The critical amplitude was in the former case 0·0051 cm., and in the latter 0·00214 cm., giving :—

	na^2/ν.	a/d.
Cylinder	0·098	0·0090
Sphere	0·56	0·0215

The value of a/d for a sphere of this order of diameter at $na^2/\nu = 0·098$ is, from the curve of fig. 8, 0·0049.

8. *Summary of Results and Conclusions.*

(1) For audible frequencies smoke particles follow closely the motion of the air in which they are suspended, and can be used as tracing points. For all except the lowest frequencies the inertia of the smallest dust particles ordinarily used in tubes is so large that they act as semi-stationary obstacles in the vibrating air.

(2) Since smoke particles follow the motion of the air they can be used to measure the amplitude of the air vibration in a tube, and hence, in conjunction with the frequency, the energy.

(3) In a tube containing a gas set in vibration by a diaphragm there is a circulation, the gas moving from antinode to node along the wall, and returning up the centre, as predicted by Lord Rayleigh. This circulation, which is very well defined if the vibration is of the vigour usual in tube experiments, has never been taken into account by those computing tube corrections of the

Kirchhoff type, and is no doubt one of the causes of the lack of agreement of computation with experiment.*

(4) Any particle which does not share the vibratory motion of the air may be the centre of a vortex motion, which is symmetrical about both a longitudinal and a transverse plane through the particle if the amplitude of vibration is uniform in the neighbourhood of the particle, but about a longitudinal plane only if the amplitude has a marked gradient. For this reason the behaviour of a particle of the inertia contemplated is no index to the movement of the air in the absence of the particle. The particle produces too much disturbance by its presence to be regarded as a test body.

(5) The principle of dynamical similarity allows us to find two non-dimensional expressions which determine whether the periodic motion of the air about an obstacle will produce vortex motion or the irrotational motion contemplated by previous workers who have treated the subject hydrodynamically. The constants have been experimentally found for different ranges of size of sphere.

(6) It is shown that in all previous experiments on the forces between spheres in vibrating air the motion, which has been tacitly assumed by the workers to be irrotational, was actually vortex motion.

I have much pleasure in acknowledging a grant from the Imperial Chemical Industries Company, expenditure from which was made in connection with this research; the special services of my assistant, Mr. L. Walden, to whose skill the clearness of the photographs is, in particular, due; and the assistance of one of my students, Mr. E. B. Pearson, in connection with the measurements.

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* *Cf.* P. S. H. Henry, "The Tube Effect in Sound-Velocity Measurements," 'Proc. Phys. Soc.,' vol. 43, p. 340 (1931).

Commutative Ordinary Differential Operators.
II.—*The Identity $P^n = Q^m$.*

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I.—*Preamble.*

In a paper previously communicated to the Society* we developed the general theory of ordinary differential operators P, Q of interprime orders m, n, which satisfy the commutative identity

$$PQ = QP.$$

Such a pair of operators also satisfy a second identity

$$f(P, Q) \equiv P^n - Q^m + \ldots = 0,$$

where, if we replace P, Q by two-way co-ordinates p, q, the equation

$$f(p, q) = 0$$

defines a curve which is integral though not necessarily rational. The expression of P, Q depends upon parameters defined by equations of Abelian form involving transcendents of genus equal to that of the curve, which, if finite double points are absent, is

$$g = \tfrac{1}{2}(m-1)(n-1).$$

If the curve possesses finite double points, operators satisfying $f(P, Q) = 0$ can still be constructed by the method of C.O.2, section IV, but the genus of the transcendents appearing will be less than $\frac{1}{2}(m-1)(n-1)$. This number, however, in virtue of its position in the theory of lattice integers, is still of considerable importance.

There is, however, a further consequence of the existence of double points. The theory of " transference " explained in C.O.2 dealt only with transference with respect to ordinary points of the fundamental curve. If all points are ordinary points the theory is complete, but, if double points are present, transference with respect to such a point invalidates the Abelian theory of transference given in C.O.2, and leads to operators not considered there.* We here illustrate these phenomena by a discussion of the *unicursal* identity $P^n = Q^m$.

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* 'Proc. Roy. Soc.' A, vol. 118, p. 557 (1928); referred to as "C.O.2." To an earlier paper, 'Proc. L. M. S.,' ser. 2, vol. 21, p. 420, *et seq.*, we refer to as "C.O.1."

In Sections II, III we enumerate the different types of solution of the identity, showing how the types may be distinguished, and how they may be connected by transference with respect to the multiple point which $p^n = q^m$ possesses at the origin. A significant feature is the appearance of *sets* of commutative operators with more than two members.

In Section IV, by discussion of a particular case, we show that the theory of C.O.2 is still valid for certain solutions of the identity, though functions, in general transcendental, are now naturally replaced by algebraic and exponential functions. In particular we identify for the case discussed the functions $\eta(p, q, x)$, $\xi(p, q, x)$, which are the common roots respectively of $P - p$, $Q - q$ and of the adjoint pair $P' - p$, $Q' - q$, and the function $\psi(p, q, x)$ ($\equiv \xi\eta$). which played an important part in the general theory.

The notational conventions and terminology are those of C.O.2, and for convenience of exposition we postpone proofs of major theorems to Section V.

II.—*The Fundamental Operators* T, U.

It is a trivial exercise to show that, if operators P, Q, U exist such that

$$UD^m = PU, \qquad UD^n = QU, \tag{1}$$

then $PQ = QP$ and

$$P^n = Q^m. \tag{2}$$

Our immediate object is to show that all solutions of (2) are known when all operators U satisfying relations of type (1) are enumerated.

If P, Q be any pair of operators satisfying (2), then, by a change of variable and a transference of order zero,† P may be reduced to standard form

$$P \equiv D^m + \mu_2 D^{m-2} + \dots .$$

Substitution in (2) shows that

$$Q \equiv D^n + \nu_2 D^{n-2} + \dots .$$

It evidently suffices to enumerate "standard solutions" of this form.

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* *Cf.* note by Professor Baker, 'Proc. Roy. Soc.,' A, vol. 118, p. 584 (1928).

† C.O.1, p. 426.

Now in Section V we show that

If P, Q is a standard solution of (2), then operators T, U exist such that

$$\mathrm{TP} = \mathrm{D}^m\mathrm{T}, \quad \mathrm{TQ} = \mathrm{D}^n\mathrm{T}\,; \quad \mathrm{PU} = \mathrm{UD}^m, \quad \mathrm{QU} = \mathrm{UD}^n\,;$$
$$\mathrm{UT} = \mathrm{P}^a\mathrm{Q}^b, \quad \mathrm{TU} = \mathrm{D}^{am+bn},$$

where a, b are positive integers. (3)

As immediate consequences we have that

Every pair of operators (P, Q) satisfying (2) may be reduced by transference and change of variable to $(\mathrm{D}^m, \mathrm{D}^n)$. (4)

We can pass by transference and change of variable from any one solution to any other. (5)

All solutions of (2) are effectively known, when we have enumerated all operators U which satisfy relations of the form (1). (6)

Revert now to (1); if $\mathrm{U} \equiv \mathrm{U}_1 f(\mathrm{D})$, where f is a polynomial with constant coefficients, then

$$\mathrm{U}_1\mathrm{D}^m \equiv \mathrm{PU}, \qquad \mathrm{U}_1\mathrm{D}^n = \mathrm{QU}_1,$$

and the transference effected by U is more simply effected by U_1. It suffices therefore to enumerate operators U which have no such end-factor. Such operators are most usefully studied through their roots. We may show that

If $\mathrm{UD}^m = \mathrm{PU}$, $\mathrm{UD}^n = \mathrm{QU}$ and U has no end-factor $f(\mathrm{D})$, then,

(i) if ζ is a root of U, so is $\mathrm{D}^{am+bn}\zeta$, where a, b are positive integers: we call $\mathrm{D}^{am+bn}\zeta$ a "lattice derivative" of ζ;

(ii) the roots of U are polynomials of different non-lattice degrees;

(iii) U is unique for a given P, Q, and, if V is any other operator such that $\mathrm{VD}^m = \mathrm{PV}$, $\mathrm{VD}^n = \mathrm{QV}$, then $\mathrm{V} = \mathrm{U}f(\mathrm{D})$. (7)

Of these results (i), (ii) are proved in Section V, while (iii) is left to the reader.

Conversely, if an operator U is known satisfying the conditions 7 (i), (ii), then, for every root ζ of U,

$$\mathrm{UD}^m\zeta = 0 = \mathrm{UD}^n\zeta,$$

and operators P, Q exist such that (1) is satisfied.

Since the non-lattice members are just g in number, it follows from 7 (ii) that

The operator U is of order not greater than g. (8)

Again, since all roots of U are polynomials, there is an integer s such that D^s annihilates all roots of U, and therefore an operator T such that

$$TU = D^s. \tag{9}$$

If s has the least possible integral value, T has no commencing factor $f(D)$.

From (1), (9) we derive

$$TP = D^m T, \qquad TQ = D^n T, \tag{10}$$

so that T is the transference-operator reducing (P, Q) to (D^m, D^n).

Denoting adjoints by " primes " we have

$$P'T' = T'(-D)^m, \qquad Q'T' = T'(-D)^n,$$

so that T′ is the U-operator appropriate to P′, Q′ and has no end-factor $f(-D)$, since T has no commencing factor $f(D)$. The order of T is the order of T′, and so by (8)

The operator T is of order not greater than g. (11)

III.—*The Significance of the Order of* U.

We indicated in the preamble that when the fundamental curve possesses double points the fundamental identity possesses various types of solution. For the identity $P^n = Q^m$ the distinction between these types is reflected in the form of U, the transference-operator giving rise to P, Q. Briefly, solutions corresponding to those discussed in C.O.2 are obtained when U is precisely of order g. Abnormalities occur when the order of U is less than g. In more detail we may show that

If U is of order g,

(i) the definition of U, P, Q involves just g disposable constants ;

(ii) P, Q have just one common root ;

(iii) any operator commutative with P, Q is of the form h (P, Q), where h is a polynomial with constant coefficients. (12)

On the other hand

If U is of order less than g,

(i) P, Q have at least two linearly independent common roots ;

(ii) there is at least one operator R commutative with P, Q and not of the form h (P, Q). (13)

We distinguish the operators of (12), (13) as of types I, II respectively. Type II contains a considerable variety of subtypes which we have not been able to classify completely to our satisfaction. In particular we are unable to assign an upper limit to the number of disposable constants occurring in their definition, though we believe it to be less than g.

We may show that, for either type,

$P - c^m$, $Q - c^n$ have just one common root $U(e^{cx})$, and transference with respect to an ordinary point of the curve transforms P, Q into operators of the same type. (14)

The relation of the distinction of types to the multiple point of the fundamental curve arises from the theorem that

Transference with respect to the origin applied to operators of type I leads to operators of type II. (15)

IV.—*A Special Pair of Solutions of* $P^n = Q^m$.

We consider the particular commutative pair

$$P \equiv x^{-m} \delta (\delta - n)(\delta - 2n) \ldots (\delta - mn + n),$$
$$Q \equiv x^{-n} \delta (\delta - m)(\delta - 2m) \ldots (\delta - mn + m),$$

where $\delta \equiv xD$, already introduced in C.O.1.*

It is easily verified that, if

$$U \equiv (\delta - j_1)(\delta - j_2) \ldots (\delta - j_g),$$
$$T \equiv x^{-2g} (\delta - l_1) \ldots (\delta - l_g),$$

where (l_s), (j_s) are respectively the lattice and non-lattice integers of the closed interval $(0, 2g - 1)$ arranged in ascending order of magnitude, then

$$UD^m = PU, \qquad UD^n = QU,$$
$$TP = D^mT, \qquad TQ = D^nT,$$
$$TU = D^{2g}.$$

By (14), $P - c^m$, $Q - c^n$ have a common root

$$\eta(c, x) = U(e^{cx}) = (\delta - j_1)(\delta - j_2) \ldots (\delta - j_g) e^{cx}, \qquad (16)$$

and clearly

The functions $\eta(\omega c, x)$, where $\omega^m = 1$, are a "normal"† set of roots of $P - c^m$. (17)

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* C.O.1, p. 425.

† C.O.2, p. 559.

We observe that the operator U removes non-lattice powers from the exponential expansion. So

The expansion of $\eta\,(c, x)$ contains only lattice powers. (18)

There are points of interest in an independent verification of (18). If we write $(\mathrm{P} - c^m)\,y = 0$ in the form

$$\delta\,(\delta - n) \ldots (\delta - mn + n)\,y = (cx)^m\,y,$$

the ordinary theory gives the series-solutions

$$y_r = \left(\frac{cx}{m}\right)^{n\,(m-r)} \sum_{t=0}^{\infty} \left[\left(\frac{cx}{m}\right)^{mt} \Big/ \prod_{s=r}^{m+r-1} \left\{\Gamma\left(n + 1 + t - \frac{sn}{m}\right)\right\}\right],$$

$(r = 1, 2, \ldots, m)$, which are found to satisfy the relations

$$c^{-n}\,\mathrm{Q}y_m = y_1, \qquad c^{-n}\,\mathrm{Q}y_r = y_{r+1} \quad (r \neq m).$$

Thus $\sum_{1}^{m} y_r$ is a solution also of $(\mathrm{Q} - c^n)\,y = 0$ and contains only lattice powers of cx.

Again, performing the operations indicated in (16), we have

$$\eta\,(c, x) = \theta\,(cx)\,e^{cx}, \tag{19}$$

where θ is a polynomial of degree g in its argument. If $c_1, c_2, \ldots, c_g$ be the zeros of $\theta\,(x)$, then the zeros of $\eta\,(c, x)$ *regarded as a function of* c are $(c_s x^{-1})$ $(s = 1, 2, \ldots, g)$ and correspond to points on the fundamental curve whose (p, q)-co-ordinates are

$$(c_s^{\,m}\,x^{-m}, \qquad c_s^{\,n}\,x^{-n}).$$

These are the " base-points " (α_s, β_s) of the commutative pair P, Q.

By substitution in the Abelian equations* we have

$$\omega_s = -\,c_s^{\,-mn+m+n}\,x^{mn-m-n-1},$$

which leads to

$$\left.\begin{aligned} &\sum_{s=1}^{g} c_s^{\,-j_r} = 0 \qquad (r = 2, 3, \ldots, g), \\ &\sum_{s=1}^{g} c_s^{\,-1} = 1. \end{aligned}\right\} \tag{20}$$

As evidence that the Abelian equations do indeed persist for the unicursal identity $\mathrm{P}^n = \mathrm{Q}^m$, we give in Section V an independent proof of (20).

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* C.O.2, p. 563 (19), (21).

From (17), (19), the normal roots of $P - c^m$ are $\theta(\omega^r cx)\exp(\omega^r cx)$. If their product be formed, exponentials disappear and

$$\Pi\{\theta(\omega^r cx)\} \equiv \Theta(c^m x^m),$$

where Θ is a polynomial of degree g in its argument. We thus have a corroboration of C.O.2, p. 575 (52).

The operators adjoint to P, Q are

$$P' \equiv (-)^m x^{-2g} P x^{2g}, \qquad Q' \equiv (-)^n x^{-2g} Q x^{2g},$$

and the common root of $P' - c^m$, $Q' - c^n$ is

$$\xi(c, x) \equiv x^{-2g}\,\theta(-cx)\,e^{-cx}.$$

If $\psi \equiv \xi\eta$, then

$$\psi(c, x) = x^{-2g}\,\theta(cx)\,\theta(-cx), \tag{21}$$

which is homogeneous of degree g in c^2, x^{-2}.

Now, by (18), the expansion of η, and similarly of ξ, contains only lattice powers of c. Hence ψ contains lattice powers of c only. This is as it should be, for $\psi(p, q, x)$ is polynomial in (p, q) and now $p, q = c^m, c^n$.

We may here remark that the operators

$$P_1 \equiv x^{-g} P x^g, \qquad Q_1 \equiv x^{-g} Q x^g.$$

are the pair contemplated in C.O.2, p. 567 (36) which transform exactly into the adjoint pair by mere change of sign of x.

Simple explicit forms for $\theta(x)$, $\psi(c, x)$ are not readily obtained. We may, however, give some which employ the auxiliary function

$$J(z) \equiv (z - j_1)(z - j_2)\dots(z - j_g).$$

For

$$\theta(x) = e^{-x} J(\delta)\, e^x = \sum_{p=0}^{\infty} \frac{(-x)^p}{p!} \sum_{q=0}^{\infty} \frac{J(q)}{q!} x^q,$$

or

$$\theta(x) = \sum_{r=0}^{g} \left\{ \sum_{p=0}^{r} \frac{(-)^p J(r-p)}{p!\,(r-p)!} \right\} x^r. \tag{22}$$

Again

$$x^{2g}\psi(c, x) = \theta(-cx)\,\theta(cx) = \sum_{p=0}^{\infty} \frac{J(p)(-cx)^p}{p!} \sum_{q=0}^{\infty} \frac{J(q)(cx)^q}{q!},$$

and, on re-arrangement,

$$\psi(c, x) = x^{-2g} \sum_{r=0}^{g} \left\{ \sum_{s=0}^{2r} \frac{(-)^s J(s)\, J(2r-s)}{s!\,(2r-s)!} \right\} (cx)^{2r}. \tag{23}$$

We may also quote without proof the formula

$$\theta(x) = \sum_{r=0}^{g} \Delta^r J(0) \frac{x^r}{r!}, \tag{24}$$

where Δ is the algebraic difference-operator.

If $m = 2$, and consequently n is odd, the differential equation $(P - c^2)y = 0$ transforms readily into Bessel's equation of order $\frac{1}{2}n$.

The common roots of $P - c^2$, $Q - (\pm c)^n$ are

$$(cx)^{\frac{1}{2}n} H^{(2)}_{\frac{1}{2}n}(icx), \qquad (cx)^{\frac{1}{2}n} H^{(1)}_{\frac{1}{2}n}(icx), \qquad (i^2 = -1)$$

respectively, the notation being that of Watson, "Bessel Functions," p. 73.

From (16) therefore

$$H^{(2)}_{\frac{1}{2}n}(icx) = C(cx)^{-\frac{1}{2}n}(\delta - 1)\ (\delta - 3) \dots (\delta - n + 2)\, e^{cx}, \tag{25}$$

where C is independent of x—an instance of the well-known fact that Bessel's functions whose order is half an odd integer are expressible finitely in terms of elementary functions.

From (20) we have

The zeros x_s of $H^{(k)}_{g+\frac{1}{2}}(x)$, where $k = 1$ or 2, are g in number and satisfy the g relations

$$\sum_{s=1}^{g} x_s^{-1} = (-)^k i,$$

$$\sum_{s=1}^{g} x_s^{-(2r+1)} = 0, \qquad (r = 1, 2, \dots, g - 1). \tag{26}$$

The expressions for θ, ψ are now more manageable. The equation

$$(P - 1)\, e^x \,\theta(x) = 0$$

gives

$$\{\delta(\delta - 2g - 1) - x^2\}\, e^x \theta(x) = 0,$$

whence

$$\{\delta(\delta - 2g - 1) + 2x(\delta - g)\}\, \theta(x) = 0.$$

Identifying $\theta(x)$ as the polynomial solution of this equation in which the term of highest degree is x^g, we obtain

$$\theta(x) = \sum_{r=0}^{g} \frac{(-)^r (g + r)!}{2^r r!\ (g - r)!} x^{g-r}. \tag{27}$$

Again, $\theta(cx)\, e^{cx}$, $\theta(-cx)\, e^{-cx}$ are both solutions of

$$\{\delta(\delta - 2g - 1) - c^2x^2\}\, y = 0.$$

The equation satisfied by products of solutions of this equation is

$$\delta(\delta - 2g - 1)(\delta - 4g - 2)z = 4c^2x^2(\delta - 2g)z.$$

We identify $x^{2g}\,\psi(c, x)$ with the polynomial solution of this equation and find

$$\psi(c, x) = c^{2g}\sum_{r=0}^{g}\frac{(-)^r(2r)!\,(g+r)!}{(r!)^2(g-r)!}(2cx)^{-2r}. \tag{28}$$

This is equivalent to the usual formula* for

$$J^2_{g+\frac{1}{2}}(x) + J^2_{-g-\frac{1}{2}}(x).$$

V.—*Proofs of Theorems.*

Enunciations are not repeated.

Proof of (3).—We require the lemma

If Y is the operator whose roots are just the roots common to the set of operators $Y_1, Y_2, \ldots$, then we can find operators $X_1, X_2, \ldots$, such that

$$Y = X_1Y_1 + X_2Y_2 + \ldots . \tag{29}$$

The proof of (29) is exactly similar to that of the analogous " H.C.F." theorem of algebra.

Now if P, Q satisfy $P^n = Q^m$ then, by C.O.1, § 2, the operators P, Q have at least one common root and so any set of operators P^aQ^b corresponding to a set of values of the integers a, b has at least one common root. Let T be the operator whose roots are common to the set P^aQ^b, where $am + bn \geqslant 2g$, and, to specify T completely, let it be written with the leading coefficient unity. Then, by the lemma,

$$T = \Sigma X_{ab}P^aQ^b \qquad (am + bn \geqslant 2g).$$

The operators $P^{a+1}Q^b$, P^aQ^{b+1} also possess T as an end-factor and so we have

$$TP = \Sigma X_{ab}P^{a+1}Q^b = P_1T, \qquad TQ = Q_1T, \tag{30}$$

where P_1, Q_1 are certain operators. By the elementary theory of transference P_1, Q_1 are commutative and $P_1{}^n = Q_1{}^m$. Again, let $mn - 1$, which is lattice,† be $cm + dn$, where $0 < c < n$, $0 < d < m$. Then

$$2g - 2 = mn - m - n - 1 = (c-1)m + (d-1)n,$$

and consequently

$$a \geqslant c \quad \text{and/or} \quad b \geqslant d.$$

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* Watson, " Bessel's Functions," p. 297.

† C.O.2, p. 561 (11).

If $a \geqslant c$, then $m(a-c)+n(b+m-d) = am+bn+1 > 2g$, and $P^{a-c}Q^{b+m-d}$ has T as an end-factor. Similarly, if $b \geqslant d$, then $P^{a+n-c}Q^{b-d}$ has T as an end-factor. In either case.

$P^{a+n}Q^b \equiv P^a Q^{b+m}$ has TP^cQ^d as an end-factor. Thus

$$TP^n = \Sigma X_{ab} P^{a+n} Q^b = CTP^cQ^d; \qquad (31)$$

where, on counting dimensions, we find that C is a linear operator. Substituting in (31)

$$P \equiv D^m + \mu_2 D^{m-2} + \dots , \qquad Q \equiv D^n + \nu_2 D^{n-2} + \dots ,$$
$$T \equiv D^r + \alpha_1 D^{r-1} + \dots,$$

we find without difficulty

$$C \equiv D.$$

Hence

$$TP^n = DTP^cQ^d. \qquad (32)$$

Employing (30) we may write (32) as

$$P_1{}^n T = DP_1{}^c Q_1{}^d T,$$

i.e.,

$$P_1{}^n = DP_1{}^c Q_1{}^d.$$

Since P_1, Q_1 are commutative, D is also commutative with them and we have

$$P_1{}^{mn} = D^m P_1{}^{cm} Q_1{}^{dm} = D^m P_1{}^{cm+dn},$$

whence

$$P_1 = D^m,$$

and similarly

$$Q_1 = D^n.$$

Thus (30) becomes

$$TP = D^m T, \qquad TQ = D^n T.$$

If $2g = a_0 m + b_0 n$, then

$$P^{a_0} Q^{b_0} = UT,$$

where U is some operator. We therefore have

$$TUD^m T = TUTP = TP^{a_0+1} Q^{b_0} = D^{a_0 m + m + b_0 n} T,$$

or

$$TU = D^{a_0 m + b_0 n}. \qquad (33)$$

Finally, from (33),

$$TUD^m = D^m TU = TPU,$$

or

$$UD^m = PU,$$

and similarly

$$UD^n = QU.$$

Proof of 7 (*i*), (*ii*).—(i) If ζ is a root of U

$$UD^m(\zeta) = PU(\zeta) = 0$$
$$= UD^n(\zeta), \quad \text{similarly}.$$

Thus $D^m(\zeta)$, $D^n(\zeta)$ are roots of U and so, more generally, is every non-vanishing $D^{am+bn}(\zeta)$.

(ii) If ζ is a root of U, so also are $D^m\zeta$, $D^{2m}\zeta$, ... Since the number of linearly independent roots of U is finite, there is a relation

$$h(D^m)\,\zeta = 0,$$

where h is a polynomial with constant coefficients. Hence

$$\zeta = \xi_0 + \sum_{r,\,s} \xi_{rs}\, e^{a_{rs}x}, \tag{34}$$

where every ξ is polynomial and the a's are constants divisible into sets such that $a_{rs}{}^m = k_r$ for every s. We show that, if exponential terms occur in (34), then, contrary to hypothesis, U has an end-factor $f(D)$.

The operator

$$h_1(D^m) \equiv \frac{h(D^m)}{D^m - k_1}$$

is polynomial in D^m and $h_1(D^m)\,\zeta$ is a root of U. The operator annihilates all terms on the right of (34) save those with exponents a_{1s} and it replaces the polynomial coefficients of these by constants. Thus U has a solution

$$\zeta_1 = h_1(D^m)\,\zeta = \sum_{s=1}^{m} c_s e^{a_{1s}x} \qquad (a_{1s}{}^m = k_1), \tag{35}$$

where not every c_s is zero. Suppose c_1 is not zero and operate on (35) with

$$\prod_{s=2}^{m} (D^n - a_{1s}{}^n).$$

Then

$$\zeta_2 \equiv \prod_{s=2}^{m} (D^n - a_{1s}{}^n)\,\zeta_1 = c_1 \prod_{s=2}^{m} (a_{11}{}^n - a_{1s}{}^n)\, e^{a_{1s}x}$$

is a root of U of the form Ae^{ax}, and U has an end-factor $D - a$, contrary to hypothesis. Again, if ζ is polynomial of lattice degree $am + bn$, then

$$0 = UD^{am+bn}(\zeta) = U\ (\text{constant}),$$

and U has an end-factor D. Thus every root is a polynomial of non-lattice degree. If two roots are of the same degree, some linear combination of them is of lower degree and so there is a fundamental system of roots of U of *different* non-lattice degrees.

Proof of (12).—(i) There are just g lattice integers l, including zero, in the closed intervals $(0, 2g-1)$ and just g non-lattice integers j, of which $2g-1$ is the largest.* We observe also that $2g-1-l$ is non-lattice and, more generally $j-l$ is non-lattice, if $l < j$.

Since U is of order g, it has roots of every non-lattice degree, and in particular a root

$$\zeta = x^{2g-1} + \Sigma k_l x^l \tag{36}$$

of degree $2g-1$ from which we suppose all other non-lattice powers removed by subtraction of constant multiples of other roots. The numbers of constants k_l is thus g. Now the lattice derivatives $D^l(\zeta)$, which, by 7 (i) are all roots of U, furnish roots of all other non-lattice degrees and form with ζ a complete set of roots of U. Thus the constants k_l, and these only, enter into the definition of U, P, Q.

(ii) We observe that, if l is *any* lattice number $am + bn$ other than zero, then at least one of the numbers $l-m$, $l-n$ is lattice.

Let ζ_j denote the polynomial root of U of degree j, and η any common root of P, Q. Let θ be any solution of $U(\theta) = \eta$. Then

$$UD^m(\theta) = PU(\theta) = P\eta = 0 = UD^n(\theta)$$

similarly. Clearly θ is polynomial and we may write it in the form

$$\theta = \Sigma c_j \zeta_j + \Sigma d_l x^l,$$

where the second summation contains only lattice powers. Of these let l_0 be the largest index.

By 7 (i), $UD^m(\zeta_j) = 0$ and so

$$0 = UD^m(\theta) = U(\Sigma d_{l1}\, x^{l-m})$$

$$0 = UD^n(\theta) = U(\Sigma d_{l2}\, x^{l-n}).$$

Thus, if l_0 is not zero, U has at least one root of lattice degree, which is impossible; $\Sigma d_l x^l$ therefore reduces to a constant term, and we have

$$\theta = \Sigma c_j \zeta_j + \text{constant},$$

whence

$$\eta = U(\theta) = U\,(\text{constant}).$$

Thus U (constant) is the only common root of P, Q.

(iii) Let R be an operator commutative with P, Q, then

$$RUD^m = RPU = PRU, \qquad RUD^n = RQU = QRU,$$

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* C.O.2, p. 570.

and so, by 7 (iii),

$$\mathrm{RU} = \mathrm{U}f(\mathrm{D}) = \mathrm{U}\{\Sigma c_l \mathrm{D}^l + \Sigma c_j \mathrm{D}^j\},$$

where f has been separated into lattice and non-lattice powers. If ζ be defined by (36),

$$\mathrm{U}(\zeta) = 0 = \mathrm{UD}^l(\zeta), \qquad \text{whether } l \gtrless 2g-1,$$

and so

$$\mathrm{U}\{\Sigma c_j \mathrm{D}^j\}\,\zeta = 0.$$

But this imputes to U a root of lattice degree $2g-1-j_0$, where j_0 is the smallest non-lattice number occurring, and U has no such root. Thus every $c_j = 0$ and

$$\mathrm{RU} = \mathrm{U}\Sigma c_l \mathrm{D}^l = \mathrm{U}\Sigma c_{ab}\mathrm{D}^{am+bn} = \Sigma c_{ab}\,\mathrm{P}^a\mathrm{Q}^b\mathrm{U},$$

i.e.,

$$\mathrm{R} = \Sigma c_{ab}\,\mathrm{P}^a\mathrm{Q}^b.$$

Proof of (13).—(i) We use the easily established result that

If j is a non-lattice integer less than $2g-1$, then one of the integers $j+m$, $j+n$ is non-lattice. (37)

Let j ($< 2g-1$) be the degree of ζ, the polynomial root of U of highest degree. Then

$$\mathrm{PUD}^{-m}(\zeta) = \mathrm{UD}^m\mathrm{D}^{-m}(\zeta) = \mathrm{U}(\zeta) = 0, \tag{38}$$

and similarly $\mathrm{QUD}^{-n}(\zeta) = 0$.

Now, by (37), one of $\mathrm{D}^{-m}(\zeta)\ \mathrm{D}^{-n}(\zeta)$ is of non-lattice degree; let it be the former and write

$$\mathrm{D}^{-m}(\zeta) \equiv \eta.$$

Since U has no root of degree $j+m$, $\mathrm{U}(\eta) \neq 0$, and there is therefore a *positive* integer r such that

$$\mathrm{UD}^{rn}(\eta) = 0, \qquad \mathrm{UD}^{(r-1)n}(\eta) \neq 0.$$

Since $\mathrm{D}^{(r-1)n}(\eta)$ is of non-lattice degree, then $\mathrm{UD}^{(r-1)n}(\eta)$ is distinct from U (constant), an obvious common root of P, Q, and is itself a common root of these operators.

For $\mathrm{QUD}^{(r-1)n}(\eta) = \mathrm{UD}^{rn}(\eta) = 0$ and

$$\mathrm{PUD}^{(r-1)n}(\eta) = \mathrm{PQ}^{r-1}\,\mathrm{U}(\eta) = \mathrm{Q}^{r-1}\,\mathrm{PU}(\eta) = 0$$

by (38).

(ii) If U is of order less than g, its roots are all of degrees less than $2g-1$; thus D^{2g-1} and, *a fortiori*, UD^{2g-1} annihilates every root of U, and an operator R exists such that

$$\mathrm{UD}^{2g-1} = \mathrm{RU}.$$

R, being of non-lattice order $2g - 1$, is clearly not expressible as h (P, Q), but it is commutative with P, Q. For

$$\mathrm{PRU} = \mathrm{PUD}^{2g-1} = \mathrm{UD}^m \, \mathrm{D}^{2g-1} = \mathrm{RUD}^m = \mathrm{RPU}.$$

Thus PR = RP and similarly QR = RQ.*

Proof of (14).—From (1)

$$\mathrm{U}\,(\mathrm{D}^m - c^m) = (\mathrm{P} - c^m)\,\mathrm{U},$$

so

$$(\mathrm{P} - c^m)\,\mathrm{U}e^{\omega cx} = 0 \qquad (\omega^m = 1).$$

Since U has no exponential root, the functions $\mathrm{U}e^{\omega cx}$ are linearly independent and furnish a complete set of roots of $\mathrm{P} - c^m$; similarly for $\mathrm{Q} - c^n$. Evidently the only common root is $\mathrm{U}e^{cx}$.

Let V be the *linear* operator annihilating this root, then† operators P_1, Q_1, exist such that

$$\mathrm{VP} = \mathrm{P}_1\mathrm{V}, \quad \mathrm{VQ} = \mathrm{Q}_1\mathrm{V}, \quad \mathrm{P}_1{}^n = \mathrm{Q}_1{}^m.$$

From $\mathrm{VU}\,(e^{cx}) = 0$ we have

$$\mathrm{VU} = \mathrm{U}_1\,(\mathrm{D} - c),$$

for some U_1 of the same order as U. If ζ is any root of U, then $\zeta - c^{-1}\,\zeta'$ is a root of U_1, of the same non-lattice degree and U_1 is of the same order and type as U. Moreover

$$\begin{aligned}\mathrm{U}_1\mathrm{D}^m\,(\mathrm{D} - c) = \mathrm{U}_1\,(\mathrm{D} - c)\,\mathrm{D}^m = \mathrm{VUD}^m &= \mathrm{VPU} \\ &= \mathrm{P}_1\mathrm{VU} = \mathrm{P}_1\mathrm{U}_1\,(\mathrm{D} - c).\end{aligned}$$

So $\mathrm{U}_1\mathrm{D}^m = \mathrm{P}_1\mathrm{U}_1$, $\mathrm{U}_1\mathrm{D}^n = \mathrm{Q}_1\mathrm{U}_1$, and P_1, Q_1 are of the same type as P, Q.

Proof of (15).—Let U be of order g, then the common root of P, Q is U (constant). Let V be a linear operator such that

$$\mathrm{VU}\ (\text{constant}) = 0.$$

If $m < n$, then U has roots of non-lattice degrees 1 to $m - 1$ and VU has an additional root of degree 0. Thus

$$\mathrm{VU} = \mathrm{U}_1\mathrm{D}^m.$$

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* Though R is not expressible as h (P, Q) it may be expressible rationally and integrally in terms of these and other operators. Thus *e.g.*, if D^j ($j = 2g - 1 - am - bn$) annihilates all roots of U, $\mathrm{UD}^j = \mathrm{SU}$ defines an S commutative with P, Q and such that $\mathrm{R} = \mathrm{P}^a\mathrm{Q}^b\mathrm{S}$. The important point is the existence of *some set* of at least three operators.

† C.O.1, p. 424.

If now $VP = P_1V$, $VQ = Q_1V$, then

$$P_1U_1D^m = P_1VU = VPU = VUD^m = U_1D^{2m},$$

and $P_1U_1 = U_1D^m$ and likewise $Q_1U_1 = U_1D^n$. Thus the U-operator appropriate to P_1, Q_1, is of order $g - m + 1$ at most and P_1, Q_1 are of type II.

Proof of (20).—

If $c_1, c_2, \ldots, c_g$ are zeros of $\theta(x)$ then

$$\sum_{s=1}^{g} c_s^{-j_r} \equiv s(j_r) = 0 \qquad (r = 2, 3, \ldots, g)$$

$$\sum_{s=1}^{g} c_s^{-1} \equiv s(1) = 1.$$

We have

$$\theta(x) = e^{-x}\eta(x), \qquad \theta'(x) = e^{-x}(\eta' - \eta),$$

and

$$\frac{x\eta'}{\eta} = x + x\frac{\theta'(x)}{\theta(x)}$$

$$= x - \sum_{s=1}^{g} \frac{xc_s^{-1}}{1 - xc_s^{-1}} = x - \sum_{r=1}^{\infty} s(r)\,x^r.$$

Now the infinite expansion of $\eta(x)$, and therefore of $x\eta'(x)$, contains only lattice powers 0, $am + bn$. In the division of $x\eta'$ by η the successive remainders and terms of the quotient can therefore contain only lattice powers. The absence of non-lattice powers from $x - \Sigma\, s(r)\, x^r$ establishes (20).

On Finite Sequences of Real Numbers.

By H. B. Heywood.

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1. *Introductory.*

The material of the science of statistics consists in the main of finite sets of numbers, which, since they are recorded in order, are sequences. They may be regarded as functions of the rank of their elements, and theorems concerning real functions hold good for them. In particular they are capable of partition, orthogonal or other, of development analogous to expansion in series and of transformation ; sets of such sequences may likewise be subjected to substitution. These considerations bring certain parts of the theory of statistics into line with general mathematical theory and suggest interesting possibilities.

The so-called theory of "factors," put forward by Spearman in connection with his researches into intelligence, has become very important in recent years.* It is an outgrowth of the theory of partial correlation.† Mathematically speaking the "factors" of a sequence are components resulting from orthogonal partition, orthogonal sequences being those which have zero correlation. In considering how far the "factors" or other components of a sequence of measurements represent physical realities, the statistician has to make a careful study of questions of distribution and sampling, but from what has been said it will be seen that the general theory of the partition and development of sequences, which is the subject of this paper, does not involve these questions. A brief discussion of the application of this method was given in a letter in 'Nature' in which the following results were indicated.‡

While this paper is a single analytical argument, each part of which is necessary to the whole, some of the theorems in the earlier sections either are known or have been tacitly assumed, but mostly in a less general form. In section 3 some propositions of analysis are applied to sequences. The partitions which are treated generally in section 4 are a conception which has been discussed under " group factors " by Godfrey Thomson and others ; the great freedom with which such partitions may be made does not seem to have been fully appreciated. Section 5 summarises some properties of the discriminant of a set of sequences ; the discriminant, together with the regression-equation of section 6 will be found in the works of Pearson and Yule. Sections 7 and 8 contain new existence theorems which I believe to be of fundamental importance. Section 9, dealing with Spearman's hierarchy, has a separate introduction.

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* A summary of the theory of factors will be found in "The Theory of Factors," Stuart C. Dodd, 'Psychological Review,' 1928, Nos. 3 and 4. Spearman's theory of intelligence is expounded in "The Abilities of Man," Macmillan, 1927 ; a discussion of this theory of intelligence occupies chapters 9, 10 and 11 of "The Essentials of Mental Measurement," William Brown and Godfrey H. Thomson, Cambridge University Press, 1925.

† G. Udny Yule, 'Proc. Roy. Soc.,' A, vol. 79, p. 182 (1907).

‡ 'Nature,' p. 306, February 28, 1931.

I have to thank Professor Filon, who was kind enough to read portions of this paper and whose comments led to some important improvements.

2. *Definitions and Explanations.*

All numbers in this paper are real ; all series and sequences are finite.

The notation $\mathbf{x}_1$ denotes the sequence of N elements $x_{11}, x_{12}, x_{13}, \ldots, x_{1N}$, that is, N values of the variate x_1 ; the order of the elements is considered inalterable. The set of all such sequences of N elements is denoted by Ω.

The sum $\Sigma_1^N x_{1q} x_{2q}$ is written $\mathbf{x}_1 \cdot \mathbf{x}_2$.

The matrix

$$\left|\begin{matrix} x_{11} & x_{12} & \cdots & x_{1N} \\ x_{21} & x_{22} & \cdots & x_{2N} \\ \cdot & \cdot & \cdot & \cdot \\ x_{n1} & x_{n2} & \cdots & x_{nN} \end{matrix}\right|$$

is indicated by $\| x_{nN} \|$.

All sequences are, unless otherwise stated, assumed to have been standardised, that is, their mean has first been deducted from each element, and the resulting elements have then been divided by the square root of the sum of their squares ; so that

$$\Sigma_p x_{pq} = 0, \qquad \Sigma_q x_{pq}{}^2 \equiv \mathbf{x}_p \cdot \mathbf{x}_p = 1. \tag{2.1}$$

In this form sequences are sometimes said to be expressed in " standard deviation measure." The sequences so standardised form a sub-set ω of the set Ω. The product-moment correlation coefficient

$$\Sigma \{(x_{1p} - \bar{x}_1)(x_{2p} - \bar{x}_2)\}/\sqrt{\{\Sigma (x_{1p} - \bar{x}_1)^2 \times \Sigma (x_{2p} - \bar{x}_2)^2\}}$$

of two sequences $\mathbf{x}_1$, $\mathbf{x}_2$ is not affected by standardisation, and in these conditions it is $\mathbf{x}_1 \cdot \mathbf{x}_2$.

The sequences $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$ are said to be independent when no relation exists of the form

$$\alpha_1 \mathbf{x}_1 + \alpha_2 \mathbf{x}_2 + \ldots + \alpha_n \mathbf{x}_n = 0. \tag{2.2}$$

This equation means a set of N linear equations with the same coefficients $\alpha_1, \alpha_2, \ldots, \alpha_n$ involving the first, the second, etc., elements of the sequences.

If the sequences $\boldsymbol{\phi}_1$, $\boldsymbol{\phi}_2$ satisfy the condition $\boldsymbol{\phi}_1 . \boldsymbol{\phi}_2 = 0$, that is, if their correlation coefficient is zero, they are said to be orthogonal. Such sequences are sometimes spoken of as "independent," but I shall reserve this term for the linear independence defined above.

When $\mathbf{x}_1 . \mathbf{x}_2 = 1$, the two sequences are identical.

A sub-set $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$, such that there exists no sequence $\boldsymbol{\phi}$ of ω for which $\mathbf{x}_p . \boldsymbol{\phi} = 0$ for all p's, is said to be complete.

3. *Series of Sequences.*

I. *Mutually orthogonal sequences are independent.*—Let $\boldsymbol{\phi}_1, \boldsymbol{\phi}_2, \ldots, \boldsymbol{\phi}_n$ be mutually orthogonal and suppose that

$$\alpha_1\boldsymbol{\phi}_1 + \alpha_2\boldsymbol{\phi}_2 + \ldots + \alpha_n\boldsymbol{\phi}_n = 0. \tag{3.1}$$

Multiply through by $\boldsymbol{\phi}_1$; since $\boldsymbol{\phi}_1 . \boldsymbol{\phi}_1 = 1$, $\boldsymbol{\phi}_1 . \boldsymbol{\phi}_q = 0$ $(q \neq 1)$, we get $\alpha_1 = 0$ and similarly $\alpha_2 = \alpha_3 = \ldots = 0$.

(All sequences of ω are orthogonal to the sequence 1, 1, ... , 1.)

II. *It is possible for* N — 1 *sequences but no more to be mutually orthogonal.*—The proof of this proposition involves a method of construction for such sets of sequences.

Let $\boldsymbol{\phi}_1, \boldsymbol{\phi}_2, \ldots, \boldsymbol{\phi}_n$ be mutually orthogonal, and attempt to find $\boldsymbol{\psi}$ orthogonal to all. For this we must have

$$\left.\begin{aligned} \psi_1 + \psi_2 + \ldots + \psi_N &= 0 \\ \phi_{11}\psi_1 + \phi_{12}\psi_2 + \ldots + \phi_{1N}\psi_N &= 0 \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot & \\ \phi_{n1}\psi_1 + \phi_{n2}\psi_2 + \ldots + \phi_{nN}\psi_N &= 0 \end{aligned}\right\} \tag{3.2}$$

$n + 1$ homogeneous linear equations.

The determinants of the matrix

$$\left|\begin{array}{ccccc} 1 & 1 & 1 & & 1 \\ \phi_{11} & \phi_{12} & \phi_{13} & \cdots & \phi_{1N} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \phi_{n1} & \phi_{n2} & \phi_{n3} & \cdots & \phi_{nN} \end{array}\right|$$

do not all vanish, for if the matrix is squared by rows we get the determinant

$$\begin{vmatrix} N & 0 & 0 & \dots & 0 \\ 0 & 1 & 0 & \dots & \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \dots & 1 \end{vmatrix} = N,$$

and this determinant is equal to the sum of the squares of the determinants of the matrix.

Hence it is possible to find $\psi_1, \psi_2, \dots, \psi_N$ not all zero if and only if $n < N - 1$. ψ when found may be standardised.

A set of N — 1 orthogonal sequences is complete.

III. *Any sequence can be expressed uniquely as a linear function of any* N — 1 *mutually orthogonal sequences.*—Let any sequence y have correlation coefficients $r_1, r_2, \dots, r_{N-1}$ with a set of N — 1 mutually orthogonal sequences

$$\phi_1, \phi_2, \dots, \phi_{N-1}.$$

Put

$$y = r_1\phi_1 + r_2\phi_2 + \dots + r_{N-1}\phi_{N-1} + r'\phi'. \tag{3.31}$$

Multiply through by ϕ_q,

$$r_q = r_q + r'\phi' \cdot \phi_q.$$

Hence $r'\phi' \cdot \phi_q = 0$, $q = 1, 2, \dots, N - 1$. Since, by II, $\phi' \cdot \phi_q$ cannot vanish for all q's it follows that $r' = 0$ and

$$y = r_1\phi_1 + r_2\phi_2 + \dots + r_{N-1}\phi_{N-1}. \tag{3.32}$$

Cor.

$$y \cdot y = r_1^2 + r_2^2 + \dots + r_n^2 = 1. \tag{3.33}$$

IV. *It is possible to have* N — 1 *independent sequences and no more.*—This follows if the sequences considered are each expressed as linear functions of the same N — 1 mutually orthogonal sequences.

Cor.—Any set of N — 1 independent sequences is complete.

(Note that if the sequence 1, 1, ..., 1 is annexed to a complete set of N — 1 sequences belonging to ω, the result is a complete set of N sequences belonging to Ω.)

V. *Any sequence can be expressed uniquely as a linear function of* N — 1 *independent sequences.*—From IV a linear relation must exist between $x_1, x_2, \dots, x_{N-1}$, y, where $x_1, x_2, \dots, x_{N-1}$ are supposed independent. This allows y to be expressed in the required form. The expansion must be unique, for otherwise the difference of two such expansions would give a relation between $x_1, x_2, \dots, x_{N-1}$.

4. *Sets of Sequences expressed in Terms of Orthogonal Sets.*

A set of n *independent sequences can be expressed as linear functions of* n *mutually orthogonal sequences in an infinite number of ways.*

Let $\mathrm{x}_1, \mathrm{x}_2, \ldots, \mathrm{x}_n$ be n independent sequences. Put

$$\begin{aligned} \mathrm{x}_1 &= \phi_1 \\ \mathrm{x}_2 &= \beta_{21}\phi_1 + \beta'_{22}\mathrm{x}_2' \\ \mathrm{x}_3 &= \beta_{31}\phi_1 + \beta'_{32}\mathrm{x}_3', \end{aligned}$$

where $\beta_{21} = \mathrm{x}_2 \,.\, \phi_1$, $\beta_{31} = \mathrm{x}_3 \,.\, \phi_1, \ldots$, all these quantities being less than unity. Then on multiplying these equations through by ϕ_1 it follows that $\mathrm{x}_2' \,.\, \phi_1 = \mathrm{x}_3' \,.\, \phi_1 = \ldots = 0$.

It is also clear that $\mathrm{x}_2', \mathrm{x}_3', \ldots$, are linearly independent, for a relation between them would imply a relation between $\mathrm{x}_1, \mathrm{x}_2, \ldots, \mathrm{x}_n$.

Proceed in the same way with $\mathrm{x}_2', \mathrm{x}_3', \ldots, \mathrm{x}_n'$.

We shall have

$$\left.\begin{aligned} \mathrm{x}_1 &= \phi_1 \\ \mathrm{x}_2 &= \beta_{21}\phi_1 + \beta_{22}\phi_2 \\ \mathrm{x}_3 &= \beta_{31}\phi_1 + \beta_{32}\phi_2 + \beta'_{33}\mathrm{x}_3'' \\ \mathrm{x}_4 &= \beta_{41}\phi_1 + \beta_{42}\phi_2 + \beta'_{43}\mathrm{x}_4'' \end{aligned}\right\} \tag{4.1}$$

where ϕ_2, being equal to x_2', is orthogonal to ϕ_1 and also to $\mathrm{x}_3'', \mathrm{x}_4'', \ldots$, which are independent of each other.

The process is capable of repetition stage by stage to the end, and finally $\mathrm{x}_1, \mathrm{x}_2, \ldots, \mathrm{x}_n$ will be expressed in terms of n mutually orthogonal functions $\phi_1, \phi_2, \ldots, \phi_n$.

This is one way of doing what was required, and only one way, if the order of the sequences is preserved.

Now perform any linear substitution on $\mathrm{x}_1, \mathrm{x}_2, \ldots$. The set of sequences resulting $\mathrm{y}_1, \mathrm{y}_2, \ldots$, can be dealt with in the same way and by reversing the substitution we get

$$\mathrm{x}_q = \beta_{q1}\phi_1 + \beta_{q2}\phi_2 + \cdots + \beta_{qn}\phi_n \qquad q = 1, 2, \ldots, n, \tag{4.2}$$

where the ϕ's and β's are different from those above, but the same symbols have been used to avoid complication of notation.

In the substitution which comes from carrying out the process (4.1), two x's are expressed in terms of two ϕ's, three x's in terms of three ϕ's, and so on; or, otherwise stated, $\beta_{pq} = 0$, if $q > p$. This form, which is analogous to that used by Erhardt Schmidt for real functions,* will be utilised later (8.1).

If $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$ are not independent, they may be expressed in terms of a number less than n of orthogonal sequences.

It is also possible to express such a set of n sequences in terms of any number of orthogonal sequences greater than their degree of independence but less than N. The orthogonal sequences in this case are not all linear functions of the $\mathbf{x}$'s.

5. *The Discriminant of a Set of Sequences.*

If the matrix $\| x_{n\mathrm{N}} \|$ of n rows and N columns is formally squared by the rule for squaring determinants by rows, we get a determinant of order n:—

$$(\Delta^2 =) \begin{vmatrix} \mathbf{x}_1 . \mathbf{x}_1 & \mathbf{x}_1 . \mathbf{x}_2 & \cdots & \mathbf{x}_1 . \mathbf{x}_n \\ \mathbf{x}_2 . \mathbf{x}_1 & \mathbf{x}_2 . \mathbf{x}_2 & \cdots & \mathbf{x}_2 . \mathbf{x}_n \\ \cdot & \cdot & \cdot & \cdot \\ \mathbf{x}_n . \mathbf{x}_1 & \mathbf{x}_n . \mathbf{x}_2 & \cdots & \mathbf{x}_n . \mathbf{x}_n \end{vmatrix} \equiv \begin{vmatrix} 1 & r_{12} & \cdots & r_{1n} \\ r_{21} & 1 & \cdots & r_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ r_{n1} & r_{n2} & \cdots & 1 \end{vmatrix} \qquad (5.1)$$

with $r_{pq} = r_{qp}$, correlation coefficients.

This determinant may be shown to be equal to the sum of the squares of the ${}_{\mathrm{N}}\mathrm{C}_n$ determinants formed by taking combinations of n columns of the matrix.

Another form of this determinant is obtained by expressing the sequences in terms of orthogonal sequences (4.2), namely

$$(\Delta^2 =) \begin{vmatrix} 1 & \boldsymbol{\beta}_1 \cdot \boldsymbol{\beta}_2 & \cdots & \boldsymbol{\beta}_1 \cdot \boldsymbol{\beta}_n \\ \boldsymbol{\beta}_2 \cdot \boldsymbol{\beta}_1 & 1 & \cdots & \boldsymbol{\beta}_2 \cdot \boldsymbol{\beta}_n \\ \cdot & \cdot & \cdot & \cdot \\ \boldsymbol{\beta}_n \cdot \boldsymbol{\beta}_1 & \boldsymbol{\beta}_n \cdot \boldsymbol{\beta}_2 & \cdots & 1 \end{vmatrix} = \| \beta_{nn} \|^2 \qquad (5.2)$$

where the sequence notation $\boldsymbol{\beta}_p$ has been used for the sequence of n elements, $\beta_{p1}, \beta_{p2}, \ldots, \beta_{pn}$. This form is identical element by element with the preceding one, since $\boldsymbol{\beta}_p . \boldsymbol{\beta}_q = r_{pq}$.

From the last form, since $\boldsymbol{\beta}_p . \boldsymbol{\beta}_p = 1$ (3.33), it follows from Hadamard's theorem on the maximum of a determinant† that $0 \leqslant \Delta^2 \leqslant 1$.

If $\Delta = 0$ there is a relation between the sequences; if $\Delta^2 = 1$, it may be deduced from Hadamard's theorem that the sequences are orthogonal; both conditions are necessary and sufficient.

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* Erhardt Schmidt, Thesis, Göttingen (1905).

† 'Bull. Sc. Math. Astr.,' vol. 17, p. 240 (1893).

The vanishing of Δ implies the vanishing of all the ${}_{N}C_n$ determinants of the matrix, another form of the condition for dependence.

The determinant Δ^2 is sometimes called the discriminant, and I shall use this term, although perhaps it would apply more appropriately to Δ.

6. *Partial Expansion in Terms of Specified Sequences.*

If $\mathbf{y}$ and $\mathbf{x}_1$ are any two sequences, write $\mathbf{y} = r_1\mathbf{x}_1 + r_1'\boldsymbol{\phi}$, where $r_1 = \mathbf{x}_1 \cdot \mathbf{y}$. Then $\mathbf{x}_1 \cdot \boldsymbol{\phi} = 0$ and $r_1' = \pm\sqrt{(1 - r_1^2)} = \mathbf{y} \cdot \boldsymbol{\phi}$.

Any sequence $\mathbf{y}$ *can be expressed uniquely in the form*

$$\mathbf{y} = \alpha_1\mathbf{x}_1 + \alpha_2\mathbf{x}_2 + \dots + \alpha_n\mathbf{x}_n + \alpha'\boldsymbol{\phi}, \tag{6.1}$$

where $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n$ *are given independent sequences and* $\boldsymbol{\phi}$ *is orthogonal to them.*

Assume provisionally the equation (6.1) with $\boldsymbol{\phi}$ undetermined and multiply it through by $\mathbf{x}_q$

$$r_q = \alpha_1 r_{1q} + \alpha_2 r_{2q} + \dots + \alpha_n r_{nq} + \alpha'\mathbf{x}_q \cdot \boldsymbol{\phi}. \qquad (q = 1, 2, \dots, n) \tag{6.2}$$

where $r_q = \mathbf{x}_1 \cdot \mathbf{y}$ and $r_{pq} = \mathbf{x}_p \cdot \mathbf{x}_q$.

Since $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n$ are independent, by section 5,

$$\begin{vmatrix} 1 & r_{12} & \dots & r_{1n} \\ r_{21} & 1 & \dots & r_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ r_{n1} & r_{n2} & \dots & 1 \end{vmatrix} \neq 0,$$

and hence $\alpha_1, \alpha_2, \dots, \alpha_n$ can be found uniquely to satisfy

$$r_q = \alpha_1 r_{1q} + \alpha_2 r_{2q} + \dots + \alpha_n r_{nq} \qquad (q = 1, 2, \dots, n) \tag{6.3}$$

With these values and with no others

$$\mathbf{x}_q \cdot \boldsymbol{\phi} = 0 \qquad (q = 1, 2, \dots, n).$$

The sequence $\boldsymbol{\phi}$ is determinate since all other quantities in (6.1) are determinate.

If (6.1) is multiplied through by (1) $\boldsymbol{\phi}$ and (2) $\mathbf{y}$, we get

$$\alpha' = \boldsymbol{\phi} \cdot \mathbf{y} \tag{6.4}$$

$$1 = \alpha_1 r_1 + \alpha_2 r_2 + \dots + \alpha_n r_n + \alpha'^2. \tag{6.5}$$

From (6.3) and (6.5)

$$\begin{vmatrix} 1-\alpha'^2 & r_1 & r_2 & \dots & r_n \\ r_1 & 1 & r_{12} & \dots & r_{1n} \\ r_2 & r_{21} & 1 & \dots & r_{2n} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ r_n & r_{n1} & r_{n2} & \dots & 1 \end{vmatrix} = 0 \tag{6.6}$$

If we write

$$\gamma \mathbf{z} = \alpha_1 \mathbf{x}_1 + \dots, + \alpha_n \mathbf{x}_n,$$

we have $\mathbf{y} = \gamma \mathbf{z} + \alpha' \boldsymbol{\phi}$ with $\mathbf{z}$ and $\boldsymbol{\phi}$ orthogonal. Hence $\gamma^2 + \alpha'^2 = 1$, which shows that both γ^2 and α'^2 are not greater than unity.

The sequence $\alpha' \boldsymbol{\phi}$ (which does not belong to ω since $\Sigma(\alpha' \phi_p)^2 = \alpha'^2$) is called the "error" by statisticians; (6.1) is the analogue of a regression equation.

When $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n$ are mutually orthogonal

$$y = r_1 \mathbf{x}_1 + r_2 \mathbf{x}_2 + \dots + r_n \mathbf{x}_n + \alpha' \boldsymbol{\phi}$$

and

$$\alpha'^2 = 1 - \Sigma r_p{}^2.$$

7. *Sequence with given Correlation Coefficients.*

To find a sequence $\mathbf{y}$ *having given correlation coefficients* $r_1, r_2, \dots, r_n$ *with a given set of independent sequences* $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n$.

We proceed as in the last article, assuming the provisional form (6.1) for the, now hypothetical, sequence $\mathbf{y}$. As before $\alpha_1, \alpha_2, \dots, \alpha_n$ are determined by the equations (6.3), but $\alpha' \boldsymbol{\phi}$ is not now determinate because $\mathbf{y}$ is hypothetical.

α'^2 is given by (6.6) and its value must be not greater than unity. The condition

$$0 \leqslant \alpha'^2 = \square \div \Delta^2 \leqslant 1, \tag{7.1}$$

where

$$\square = \begin{vmatrix} 1 & r_1 & r_2 & \dots & r_n \\ r_1 & 1 & r_{12} & \dots & r_{1n} \\ r_2 & r_{21} & 1 & \dots & r_{2n} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ r_n & r_{n1} & r_{n2} & \dots & 1 \end{vmatrix} \tag{7.2}$$

must be satisfied.

The condition may be written

$$0 \leqslant \square \leqslant \Delta^2.$$

If this condition is satisfied, then we may take for $\boldsymbol{\phi}$ any sequence orthogonal to $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n$, and the general form of $\mathbf{y}$ will be given by (6.1); it contains an arbitrary sequence $\boldsymbol{\phi}$ but is in other respects determinate, since the positive sign may conventionally be taken for α'.

In the boundary case $\square = 0$, $\boldsymbol{\phi}$ is absent and $\mathbf{y}$ is unique; the other boundary case, $\square = \Delta^2$, corresponds to $r_1 = r_2 = \ldots = r_n = 0$, when any sequence $\boldsymbol{\phi}$ orthogonal to $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$ will satisfy the given conditions.

8. *Set of Sequences with a given Scheme of Correlation Coefficients.*

To find a set of sequences $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$, *if any, having the given array of correlation coefficients*

$$\begin{matrix} 1 & r_{12} & r_{13} & \cdots & r_{1n} \\ r_{21} & 1 & r_{23} & \cdots & r_{2n} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ r_{n1} & r_{n2} & r_{n3} & \cdots & 1 \end{matrix}$$

where $r_{pq} = r_{qp}$ *and* $\Delta_n \neq 0$.

We will take a trial set in the form (4.2) with $\beta_{pq} = 0$, $q > p$.

$$\left.\begin{aligned} \mathbf{x}_1 &= \beta_{11}\boldsymbol{\phi}_1 \\ \mathbf{x}_2 &= \beta_{21}\boldsymbol{\phi}_1 + \beta_{22}\boldsymbol{\phi}_2 \\ \mathbf{x}_3 &= \beta_{31}\boldsymbol{\phi}_1 + \beta_{32}\boldsymbol{\phi}_2 + \beta_{33}\boldsymbol{\phi}_3 \\ & \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ \mathbf{x}_n &= \beta_{n1}\boldsymbol{\phi}_1 + \beta_{n2}\boldsymbol{\phi}_2 + \ldots + \beta_{nn}\boldsymbol{\phi}_n \end{aligned}\right\} \tag{8.1}$$

where $\boldsymbol{\phi}_1, \boldsymbol{\phi}_2, \ldots, \boldsymbol{\phi}_n$ are mutually orthogonal and $\beta_{11} = 1$.

If this set satisfies the conditions, then

$$\begin{vmatrix} \beta_{11} & 0 & 0 & \ldots & 0 \\ \beta_{21} & \beta_{22} & 0 & \ldots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \beta_{n1} & \beta_{n2} & \beta_{n3} & \cdots & \beta_{nn} \end{vmatrix}^2 \equiv \begin{vmatrix} 1 & r_{12} & \cdots & r_{1n} \\ r_{12} & 1 & \ldots & r_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ r_{n1} & r_{n2} & \cdots & 1 \end{vmatrix} = \Delta^2 \tag{8.2}$$

identically, that is element by element after squaring the left-hand side by rows.

This is true also for each partial discriminant.

$$\begin{vmatrix} \beta_{11} & 0 & \ldots & 0 \\ \beta_{21} & \beta_{22} & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ \beta_{p1} & \beta_{p2} & \cdots & \beta_{pp} \end{vmatrix}^2 = \begin{vmatrix} 1 & r_{12} & \cdots & r_{1p} \\ r_{21} & 1 & \ldots & r_{2p} \\ \cdot & \cdot & \cdot & \cdot \\ r_{p1} & r_{p2} & \cdots & 1 \end{vmatrix} = \Delta_p^2, \quad p \leqslant n. \tag{8.3}$$

Hence $\Delta_p^2 = \beta_{11}^2 \beta_{22}^2 \dots \beta_{pp}^2$, giving

$$\beta_{pp}^2 = \Delta_p^2/\Delta_{p-1}^2. \tag{8.4}$$

Since $0 < \beta_{pp}^2 \leqslant 1$, $p = 1, 2, \dots, n$, it follows that

$$0 < \Delta^2 \leqslant \Delta_{n-1}^2 \dots \leqslant \Delta_p^2 \dots \leqslant \Delta_2^2 \leqslant 1. \tag{8.5}$$

This is a necessary condition.

Conversely if (8.5) is satisfied, possible values of $\beta_{11}^2, \beta_{22}^2, \dots, \beta_{nn}^2$ can be found and it remains to find β_{21}; β_{31}, β_{32}; ... .

This can be done formally from the relations

$$\mathbf{x}_1 . \mathbf{x}_2 = r_{12}; \qquad \mathbf{x}_1 . \mathbf{x}_3 = r_{13}, \qquad \mathbf{x}_2 . \mathbf{x}_3 = r_{23}; \dots$$

which permit β_{21}; β_{31}, β_{32}; $\beta_{41}, \beta_{42}, \beta_{43}$; ..., to be found in this order and give

$$\beta_{21} = r_{21} = r_{12};$$
$$\beta_{31} = r_{31}, \quad \beta_{32} = (r_{32} - \beta_{21}\beta_{31})/\beta_{22}$$
$$\beta_{41} = r_{41}, \quad \beta_{42} = (r_{42} - \beta_{21}\beta_{31})/\beta_{22}, \quad \beta_{43} = (r_{43} - \beta_{31}\beta_{41} - \beta_{32}\beta_{42})/\beta_{33}.$$

It will be noted that, in the formal expressions so obtained, the only coefficients appearing in the denominators are $\beta_{11}, \beta_{22}, \beta_{33}, \dots$, none of which vanish; thus all the β's are finite and if the signs of $\beta_{11}, \beta_{22}, \dots$, are specified, *e.g.*, all positive, the determination is unique.

If the β's are determined successively from these equations and expressed in terms of r_{12}, r_{13}, r_{23} as far as β_{32}, it is possible to make a determination of β_{33}^2 from the relation

$$\mathbf{x}_3 . \mathbf{x}_3 = 1 = \beta_{31}^2 + \beta_{32}^2 + \beta_{33}^2, \tag{8.6}$$

and since the determination is unique, it follows that the formal expression so found will be identical with that found previously, namely, Δ_3^2/Δ_2^2; its value will be positive and not greater than unity. Thus the values found for β_{31}, β_{32}, β_{33} are consistent and appropriate. The same argument may be pursued through the whole array of coefficients and finally the whole array

$$\begin{array}{lll} \beta_{11} & & \\ \beta_{21} & \beta_{22} & \\ \beta_{31} & \beta_{32} & \beta_{33} \\ . & . & . \quad . \quad . \end{array}$$

will be determined to give the required array of correlation coefficients r_{pq}.

With these coefficients may be associated any set of n mutually orthogonal sequences $\mathbf{\phi}_1, \mathbf{\phi}_2, \ldots, \mathbf{\phi}_n$ to build up the required set $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$.

The conditions (8.5) are therefore sufficient as well as necessary.

Apart from the fact that $\mathbf{\phi}_1, \mathbf{\phi}_2, \ldots, \mathbf{\phi}_n$ are arbitrary, a circumstance which covers the ambiguous signs of $\beta_{11}, \beta_{22}, \ldots$, there is still a great deal of latitude in the β's, since we shall have a different array of β's for each of the n ! permutations of corresponding rows and columns in Δ^2. For each of these the set of determinants in (8.5) will be different.

All these forms of conditions (8.5) must be equivalent, that is, any one form implies all the others. For, having determined a set $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$, we may express this otherwise in the form (8.1) by starting with any $\mathbf{x}_p$ and taking the other $\mathbf{x}$'s in any order (§ 4). This establishes the existence of the new relative array of β's and hence the new form of the conditions (8.5).

It will be seen that the equations (8.1), $\mathbf{\phi}_1, \mathbf{\phi}_2, \ldots, \mathbf{\phi}_n$ being an arbitrary mutually orthogonal set, is a complete solution of the problem of finding $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$, since it covers all other permutations.

9. *Spearman's General Factor.*

9.1. *Explanation.*—The case where the elements in the rows (and in the columns) of the scheme of correlation coefficients of a set of sequences are in proportion is important, because this is the basis of Spearman's theory of general intelligence. In this case, subject to certain restrictions, the sequences can be expressed in the form

$$\mathbf{x}_1 = r_1\mathbf{\phi} + r_1'\mathbf{\phi}_1, \quad \mathbf{x}_2 = r_2\mathbf{\phi} + r_2'\mathbf{\phi}_2, \ \ldots, \quad \mathbf{x}_n = r_n\mathbf{\phi} + r_n'\,\mathbf{\phi}_n \qquad (9.11)$$

where $\mathbf{\phi}, \mathbf{\phi}_1, \mathbf{\phi}_2, \ldots, \mathbf{\phi}_n$ are a mutually orthogonal set of $n + 1$ sequences. I am therefore giving a complete discussion.

This case has been dealt with by Garnett*; he assumed that the sequences had normal distributions, and his paper had two further small restrictions. He excluded the case $r_{12}r_{13}/r_{23} = \kappa < 0$ (see later) because his enquiries had not revealed the existence of any instance of this case in psychological statistics; it is not an impossible case, and if indeed it does not occur, this is a significant fact. But we must not exclude the possibility that its absence may be due to the rejection by psychologists of tests regarded as unsatisfactory; as will be seen, it is associated with the occurrence of small negative correlations. Secondly, his proof that his characteristics $f(p)$ are less than unity does not cover $f(1)$, which may in fact be greater than unity. His work is therefore subject to the further condition $f(1) < 1$. The theorem breaks down when either of the conditions is not satisfied. Proceeding by a different method we shall see that the distributions are not involved and that Garnett's theorem is generally true, subject to the conditions stated, and is not true in any other case.

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* 'Proc. Roy. Soc.,' A, vol. 96, p. 91 (1919).

Spearman* dealt with the same problem and indicated without giving a formal proof that the theorem was true for distributions other than normal ones. Finally Piaggio† indicated a constructive method by which it might be shown that the theorem was generally true, and discussed briefly the error of g, the "general factor."

9.2. *Analysis of Spearman's Scheme (Hierarchy).*—Given a scheme

$$\begin{matrix} 1 & r_{12} & r_{13} & \cdots & r_{1n} \\ r_{21} & 1 & r_{23} & \cdots & r_{2n} \\ . & . & . & . & . \\ r_{n1} & r_{n2} & r_{n3} & \cdots & 1 \end{matrix} \tag{9.21}$$

satisfying the conditions

$$r_{pq} = r_{qp} \qquad r_{pq} \neq 0 \qquad |r_{pq}| < 1 \tag{9.22}$$
$$r_{pq}/r_{sq} = r_{pt}/r_{st} \qquad p \neq q \neq s \neq t;$$

apart from the elements in the leading diagonal, the elements in any two rows (columns) are proportional.

If $r_{12}, r_{13}, \ldots, r_{1n}$ are not all positive we may make them so by changing the signs of the elements in columns and rows of equal rank. We have not assumed the existence of a set of sequences with the given scheme, but may remark that if such a set exists, this process will correspond to the legitimate process of reversing the signs of all elements in certain sequences of the set.

Let the ratio of the pth row to the first row be ρ_p and put $r_{12} = k\rho_2$. The scheme may be written

$$\begin{matrix} 1 & k\rho_2 & k\rho_3 & .. & k\rho_n \\ k\rho_2 & 1 & k\rho_2\rho_3 & .. & k\rho_2\rho_n \\ k\rho_3 & k\rho_3\rho_2 & 1 & .. & k\rho_3\rho_n \\ . & . & . & . & . \\ k\rho_n & k\rho_n\rho_2 & k\rho_n\rho_3 & .. & 1 \end{matrix} \tag{9.23}$$

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* 'Proc. Roy. Soc.,' A, vol. 101, p. 94 (1922).

† 'Nature' (January 10, 1931).

It will be seen that

$$k = r_{12}\, r_{13}/r_{23}. \tag{9.24}$$

Since $k\rho_2$, $k\rho_3$, ..., are positive, if k is positive then $\rho_2, \rho_3, \ldots, \rho_n$ are positive and all the elements r_{pq} are positive.

If k is negative then all the ρ's and all the r's except those in the first row and first column are negative. In this case we reverse the signs in the first row and then in the first column and all the elements of the scheme except those in the leading diagonal will be negative.

It may be noted that k may be based on any three suffixes. Writing $k_{pq.s} = r_{ps}r_{sq}/r_{pq} = k\rho_s^2$, it follows that all k's have the same sign.

It is important also to note that r_{12}, r_{13}, r_{23} may be regarded as independent, that is, not restricted by (9.22), so that k may have any value positive or negative, except zero. Thus we distinguish the two cases.

Case 1.—$k > 0$.

Put $r_1 = +\sqrt{k}$, $r_1\rho_2 = r_2$, $r_1\rho_3 = r_3$, ..., $r_1\rho_n = r_n$.
The scheme becomes

$$\begin{array}{ccccc} 1 & r_1r_2 & r_1r_3 & \cdots & r_1r_n \\ r_1r_2 & 1 & r_2r_3 & \cdots & r_2r_n \\ \cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot \\ r_1r_n & r_2r_n & r_3r_n & \cdots & 1 \end{array} \tag{9.25}$$

where all the r's are positive and determinate.

This form of the scheme is unique, for, suppose the existence of another form with $r_1', r_2', r_3', \ldots$. From $r_1'r_2' = r_1r_2$, $r_1'r_3' = r_1r_3$, $r_2'r_3' = r_2r_3$ it follows that $r_1^2 = r_1'^2$, $r_2^2 = r_2'^2$, $r_3^2 = r_3'^2$, and since all are positive $r_1 = r_1'$, $r_2 = r_2'$, $r_3 = r_3'$.

Since r_{12}, etc., are all less than 1, it follows that no two of $r_1, r_2, \ldots, r_n$ can both be greater than 1, but one of them may be greater than 1. Hence we have, if r_1 is the greatest,

$$0 < r_1 \qquad 0 < r_p < 1 \qquad p = 2, 3, \ldots, n. \tag{9.26}$$

Case 2.—$k < 0$.

In this case we put $r_1 = +\sqrt{-k}$, $r_1\rho_2 = r_2$, $r_1\rho_3 = r_3$, and the scheme takes the form

$$\begin{array}{ccccc} 1 & -r_1r_2 & -r_1r_3 & \cdots & -r_1r_n \\ -r_1r_2 & 1 & -r_2r_2 & \cdots & -r_2r_n \\ \cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot \\ -r_1r_n & -r_2r_n & -r_3r_n & \cdots & 1 \end{array} \tag{9.27}$$

As before, the form is unique and

$$0 < r_1 \qquad 0 < r_p < 1 \qquad p = 2, 3, \ldots, n.$$

9.3. *Study of Possible Spearman Schemes.*—We have not assumed that the scheme $\| r_{pq} \|$ has arisen from a set of sequences, and we now proceed to ascertain in what circumstances a relevant set exists.

Case 1.—This discriminant is (9.25)

$$\begin{vmatrix} 1 & r_1r_2 & r_1r_3 & \cdots & r_1r_n \\ r_1r_2 & 1 & r_2r_3 & \cdots & r_2r_n \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ r_1r_n & r_2r_n & r_3r_n & \cdots & 1 \end{vmatrix} (= \Delta^2) \qquad (9.31)$$

where

$$0 < r_1 \qquad 0 < r_p < 1 \qquad p = 2, 3, \ldots, n.$$

On expanding we have

$$\Delta^2 = (1 - r_1^2)(1 - r_2^2) \ldots (1 - r_n^2)\{1 + r_1^2/(1 - r_1^2) + r_2^2/(1 - r_2^2) + \ldots + r_n^2/(1 - r_n^2)\}, \quad (9.32)$$

and

$$\Delta^2 = \Delta_1^2 - r_1^2(1 - r_2^2)(1 - r_3^2) \ldots (1 - r_n^2)\{r_2^2/(1 - r_2^2) + r_3^2/(1 - r_3^2) + \ldots + r_n^2/(1 - r_n^2)\}, \quad (9.33$$

where Δ_1^2 is the discriminant with the first row and the first column removed.

When $r_1 \leqslant 1$ (9.32) shows that Δ^2 is positive and (9.33) shows that $\Delta^2 < \Delta_1^2$. The successive application of (9.32) and (9.33) to the leading minors shows that

$$0 < \Delta^2 < \Delta_1^2 < \Delta_{12}^2 < \ldots < \Delta_{12\ldots,n-1}^2 < 1. \qquad (9.34)$$

Hence by § 8 the existence of a relevant set of sequences is established.

When $r_1 > 1$ (9.33) shows that $\Delta^2 \geqslant 0$ if

$$r_1^2 \leqslant \Delta_1^2/[(1 - r_2^2) \ldots (1 - r_n^2)\{r_2^2/(1 - r_2^2) + \ldots + r_n^2/(1 - r_n^2)\}]$$
$$= 1 + 1/\{r_2^2/(1 - r_2^2) + r_3^2/(1 - r_3^2) + \ldots + r_n^2/(1 - r_n^2)\}. \quad (9.35)$$

If this condition is satisfied, we have as before the inequalities (9.34), and a relevant set of sequences exists; otherwise no set exists.

Case 2.—The discriminant (9.26) is

$$\begin{vmatrix} 1 & -r_1r_2 & -r_1r_3 & \cdots & -r_1r_n \\ -r_1r_2 & 1 & -r_2r_3 & \cdots & -r_2r_n \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ -r_1r_n & -r_2r_n & -r_3r_n & \cdots & 1 \end{vmatrix} \qquad (9.36)$$

where

$$0 < r_1 \qquad 0 < r_p < 1 \qquad p = 2, 3, \ldots, n.$$

The equations corresponding to (9.32) and (9.33) are

$$\Delta^2 = (1 + r_1^2)(1 + r_2^2) \ldots (1 + r_n^2)\{1 - r_1^2/(1 + r_1^2) - r_2^2/(1 + r_2^2) - \ldots - r_n^2/(1 + r_n^2)\} \tag{9.37}$$

$$\Delta^2 = \Delta_1^2 - r_1^2 (1 + r_2^2) \ldots (1 + r_n^2)\{r_2^2/(1 + r_2^2) + \ldots + r_n^2/(1 + r_n^2)\}. \tag{9.38}$$

A similar discussion shows that the relevant set of sequences exists provided

$$r_1^2/(1 + r_1^2) + r_2^2/(1 + r_2^2) + \ldots + r_n^2/(1 + r_n^2) < 1. \tag{9.39}$$

It is permissible for r_1 to be greater than unity, if $r_2, r_3, \ldots, r_n$ are sufficiently small. However, the values of the elements of the scheme, r_{12}, r_{13}, etc., are very restricted. If one of the $\frac{1}{2}n(n-1)$ different elements is near to minus unity, the others must all be small; or, again, if the elements are equal their values will be less than $1/(n-1)$.

9.4. *The General Factor Established.*—Suppose now we have a set of sequences $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$ expressible in the form

$$\mathbf{x}_1 = r_1\phi + r_1'\phi_1, \quad \mathbf{x}_2 = r_2\phi + r_2'\phi_2, \ldots, \quad \mathbf{x}_n = r_n\phi + r_n'\phi_n, \tag{9.41}$$

where $\phi, \phi_1, \phi_2, \ldots, \phi_n$ are an orthogonal set of $n + 1$ sequences and therefore

$$r_1^2 + r_1'^2 = r_2^2 + r_2'^2 = \ldots = r_n^2 + r_n'^2 = 1. \tag{9.42}$$

The coefficients $r_1, r_2, \ldots, r_1', r_2', \ldots$ may be supposed all positive since the signs of $\mathbf{x}_1, \mathbf{x}_2, \ldots, \phi_1, \phi_2, \ldots$ are at our disposal. If r_1 is the greatest of the r_p's, then

$$r_1 \leqslant 1 \quad r_p < 1 \quad p = 2, 3, \ldots, n.$$

Since $r_{pq} = \mathbf{x}_p \cdot \mathbf{x}_q = r_p r_q$, we have here the scheme (9.31) with $r_1 \leqslant 1$. This form (9.41) cannot arise from any other kind of scheme.

Conversely suppose a given set of independent sequences $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$ *to have a scheme of form* (9.31) *with* $r_1 \leqslant 1$, r_1 *being the greatest of the* r_p*'s. Then* $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$ *can be expressed in the form* (9.41).

We remark that the sequence ϕ if it exists must have correlation coefficients $r_1, r_2, \ldots, r_n$ with $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$.

By § 7 such a sequence can be found if

$$0 \leqslant R \equiv \begin{vmatrix} 1 & r_1 & r_2 & \cdots & r_n \\ r_1 & 1 & r_1r_2 & \cdots & r_1r_n \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ r_n & r_1r_n & r_2r_n & \cdots & 1 \end{vmatrix} \div \Delta^2 \leqslant 1. \tag{9.43}$$

The boundary cases may be excluded.

This ratio is equal to

$$1/\{1 + r_1^2/(1 - r_1^2) + r_2^2/(1 - r_2^2) + \dots + r_n^2/(1 - r_n^2)\}, \quad (9.44)$$

and the condition is satisfied. The sequence $\boldsymbol{\phi}$ is given by

$$\boldsymbol{\phi} = \alpha_1 \mathbf{x}_1 + \alpha_2 \mathbf{x}_2 + \dots + \alpha_n \mathbf{x}_n + \alpha' \boldsymbol{\phi}', \quad (9.45)$$

where $\alpha_1, \alpha_2, \dots, \alpha_n$ are the roots of

$$\left.\begin{array}{c} r_p = \alpha_1 r_p r_1 + \alpha_2 r_p r_2 + \dots + \alpha_p + \dots + \alpha_n r_p r_n \\ p = 1, 2, \dots, n, \qquad \alpha'^2 = \mathrm{R} \end{array}\right\}, \quad (9.46)$$

and $\boldsymbol{\phi}'$ is an arbitrary sequence orthogonal to $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n$.

If now we use this sequence $\boldsymbol{\phi}$ in the equations (9.41) the required expressions are obtained, for

$$r_p r_q = \mathbf{x}_p \,.\, \mathbf{x}_q = r_p r_q + r_p' r_q' \,\boldsymbol{\phi}_p \,.\, \boldsymbol{\phi}_q,$$

so that $\boldsymbol{\phi}_p \,.\, \boldsymbol{\phi}_q = 0$.

There is no restriction on $\boldsymbol{\phi}'$ except that it is orthogonal to $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n$, and all the other constituents in the right-hand of (9.45) are determinate.

The excluded case $r_1 = 1$ may be noted. In this case $\boldsymbol{\phi} \equiv \mathbf{x}_1$ and α' is zero.

When $r_1 > 1$, it is possible to put $\mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_n$ into the required form, but $\mathbf{x}_1$ cannot be put into this form. If we put

$$\mathbf{x}_1 = r\boldsymbol{\phi} + r'\boldsymbol{\phi}_1, \qquad \mathbf{x}_2 = r_2\boldsymbol{\phi} + r_2'\boldsymbol{\phi}_2, \dots,$$

where $\boldsymbol{\phi} \,.\, \boldsymbol{\phi}_1 = 0$ and r' is positive, we have

$$\mathbf{x}_1 \,.\, \mathbf{x}_p = r_1 r_p = r r_p + r' r_p' \,\boldsymbol{\phi}_1 \,.\, \boldsymbol{\phi}_p, \qquad p = 2, 3, \dots, n,$$

whence $\boldsymbol{\phi}_1 \,.\, \boldsymbol{\phi}_p = r_p (r_1 - r)/(r' r_p')$, which is positive for every value of p.

Returning to the case where all the r_p's are less than unity, it is evident that as the number n of sequences under consideration increases, so α', the weight of the arbitrary component, diminishes; it will become small if the denominator of (9.44) becomes great, but it cannot vanish, so long as no r_p is actually equal to unity, nor can we assume without investigation that it becomes small in any given case. If one of the r_p's is equal to unity, the corresponding $\mathbf{x}_p$ will actually be $\boldsymbol{\phi}$.

The development for $\boldsymbol{\phi}$ in (9.45) changes as the number n increases, but the earlier developments include the later ones, that is to say for instance, any particular $\boldsymbol{\phi}$ appropriate for $n + 1$ sequences would also be a particular $\boldsymbol{\phi}$ appropriate for n of these sequences.

Isotherms of Hydrogen, Carbon Monoxide and their Mixtures.

By D. T. A. Townend and L. A. Bhatt, High Pressure Gas Research Laboratories of the Imperial College of Science and Technology, London.

(Communicated by W. A. Bone, F.R.S.—Received July 24, 1931.)

Introduction.

In a previous communication from these laboratories by G. A. Scott* an account was given of the determination of the isotherms of hydrogen, carbon monoxide and mixtures of the two in the molecular proportion 2 : 1, 1 : 1 and 1 : 2 over a pressure range up to 170 atmospheres and at a temperature of 25° C. Since the completion of that investigation new apparatus has been installed so that the pressure and temperature ranges might be extended; and in this paper are embodied the results of further determinations carried out at both 0° C. and 25° C. and over a pressure range extending up to 600 atmospheres. In pursuing this investigation further it is our endeavour to furnish information in regard to the gaseous mixtures in question over the pressure and temperature ranges now commonly used in industrial processes.

The Isotherms of the Single Gases.

A repetition in our new apparatus of the determinations previously made by Scott both for the single gases and gas mixtures at 25° C. and at pressures up to 170 atmospheres showed his figures to be in close agreement with our own, the variations never exceeding 0·1 per cent.

(*a*) *Hydrogen Isotherms.*—Many investigators have studied the compressibility of hydrogen at 0° C. but no independent figures at 25° C. are available other than those of Tanner and Masson† covering pressures up to 125 atmospheres. The isotherms determined in the present investigation are best expressed by the following equations :—

At 0° C.

$$pv_A = 0\cdot999347 + 0\cdot65267 \times 10^{-3}\,p + 0\cdot09192 \times 10^{-6}\,p^2 - 0\cdot0285 \times 10^{-9}\,p^3.$$

At 25° C.

$$pv_A = 1\cdot090905 + 0\cdot62183 \times 10^{-3}\,p + 0\cdot27938 \times 10^{-6}\,p^2 - 0\cdot2454 \times 10^{-9}\,p^3.$$

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* 'Proc. Roy. Soc.,' A, vol. 125, p. 330 (1929).

† 'Proc. Roy. Soc.,' A, vol. 126, p. 268 (1930).

Holborn and Otto's* figures at 0° C. and pressures up to 100 atmospheres show slight variations in each direction from our own with an average deviation of 0·35 per cent. Verschoyle's† data for the same isotherm at pressures up to 200 atmospheres are lower by an average of 0·12 per cent., the maximum deviation being 0·16 per cent. at 104 atmospheres, while the most recent figures, namely those of Bartlett‡ are higher by an average of 0·18 per cent., the maximum deviation being 0·34 per cent. at 400 atmospheres, an exception occurring at 100 atmospheres where his value is lower by 0·15 per cent.

(*b*) *Carbon Monoxide Isotherms.*—Until 1929, when Scott communicated his determinations at 25° C., no reliable data were available for the compressibility of carbon monoxide. A few months later S. Botella Goig§ published figures at 0°, 12·44° and 20·22° C. over a pressure range up to 130 atmospheres, and soon afterwards Bartlett|| published the results of an extensive investigation covering temperatures between —70° and 200° C. and pressures up to 1000 atmospheres.

The equations best expressing the isotherms determined in the present investigation are:—

At 0° C.

$$pv_A = 1{\cdot}000729 - 0{\cdot}73386 \times 10^{-3}p + 4{\cdot}72196 \times 10^{-6}p^2 - 3{\cdot}4452 \times 10^{-9}\,p^3.$$

At 25° C.

$$pv_A = 1{\cdot}091825 - 0{\cdot}44569 \times 10^{-3}\,p + 3{\cdot}98143 + 10^{-6}\,p^2 - 2{\cdot}9657 \times 10^{-9}\,p^3.$$

Bartlett's figures are higher by an average of 0·4 per cent. at 0° C. and 0·35 per cent. at 25° C., while those of Goig at 0° C. are hardly 0·03 per cent. lower than those recorded herein.

Experimental.

Apparatus and Method.—The method employed in these investigations consists in filling with the gas or mixture under investigation a vessel of known constant volume, the temperature being known and constant and the gas pressure accurately measured, and upon releasing the gas measuring its volume

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* 'Z. Physik,' vol. 23, p. 77 (1924); vol. 33, p. 1 (1925).

† 'Proc. Roy. Soc.,' A, vol. 111, p. 552 (1926).

‡ 'J. Amer. Chem. Soc.,' vol. 50, p. 1275 (1928).

§ 'Ann. Soc. Espan. Fis. Quim.,' vol. 27, p. 315 (1929); also 'C. R. Acad. Sci. Paris,' vol. 189, p. 246 (1929).

|| 'J. Amer. Chem. Soc.,' vol. 52, p. 1374 (1930).

at atmospheric pressure. For reasons previously referred to* this method has considerable advantages over others when determinations at high pressures are being made. The apparatus, which consisted essentially of (i) a high pressure vessel together with its filling system; (ii) an accurate pressure balance; and (iii) a glass measuring system contained in a water bath fitted with a plate-glass window which was maintained at a constant temperature of 25° C. and in which (for determinations at 25° C.) the high pressure vessel was also immersed, was essentially as described by Scott but with the following alterations :—

(i) *The high pressure vessel* (fig. 1) was now a nickel steel cylinder 40 cm. in length and 7·5 cm. in external diameter, with a cavity A of circular section 1 cm. in diameter drilled to a depth of 33 cm., and capable of withstanding

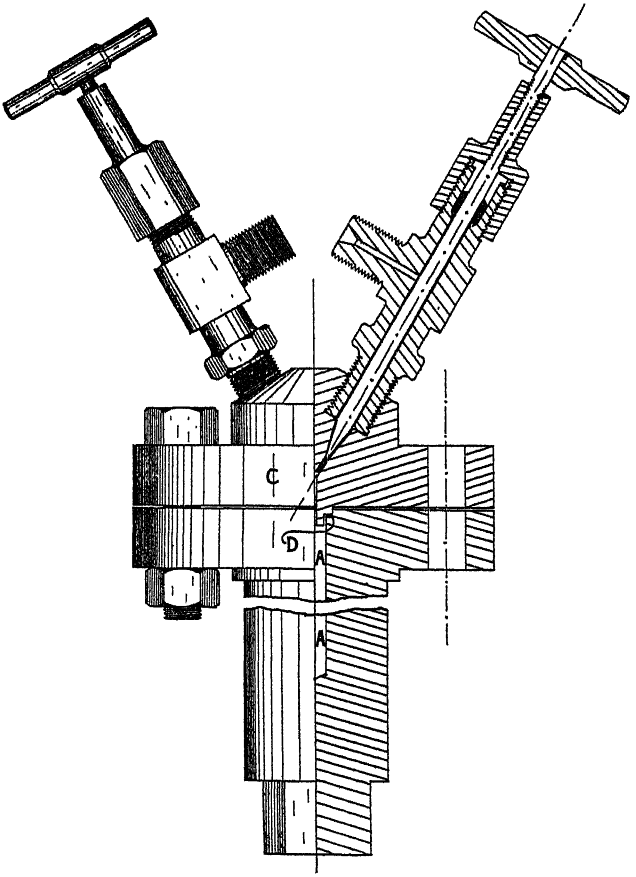

FIG. 1.

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* Scott, *loc. cit.*

an internal pressure of 3000 atmospheres. The open end of the cylinder was closed by means of a flanged head C held by eight ¾-inch bolts. Two Hofer type needle valves (one inlet and one outlet), each standing at 60° from the horizontal and from each other, were screwed into C. The vessel was rendered gas tight by means of a silver ring D resting on an annular recess turned from the head of the cylinder. It may be observed that as the level of the liquid in the constant temperature bath was always maintained well above C, even the very small volume of gas confined immediately beneath the valve seatings could be maintained at the temperature of the vessel. The volume of the vessel was determined by the method previously described and the mean of several determinations showed its value to be 27·751 c.c. at 25° C. and 27·728 c.c. at 0° C. These values were checked from time to time with the help of the known compressibility of hydrogen by measuring the volume of this gas when released from the vessel which had been previously filled to some known pressure.

The filling system (fig. 2) was similar to that used by Scott except that the first stage glycerine pump was discarded and replaced by a high pressure cylinder C in which the gas or gas mixture under investigation had been previously compressed to a pressure of about 400 atmospheres. The gas from C was (i) released through a steel tube D containing in one-half of its length highly purified phosphorus pentoxide and in the other activated cocoanut shell charcoal, and (ii) by means of valve E allowed to pass both to

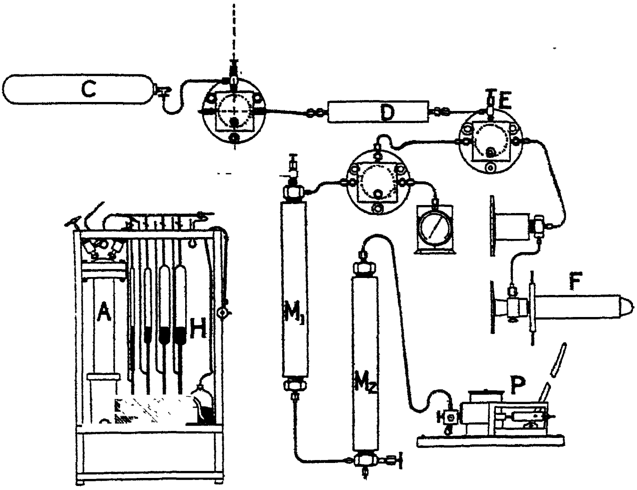

FIG. 2.

the pressure balance F and to the mercury pump M_1. After connecting M_1 to the high pressure vessel A and closing E, the final compression was effected by raising mercury from M_2 into M_1 by means of the pump P. Steel capillary tubes, screwed into mild steel union nipples and rendered gas tight by means of silver brazing, were used throughout the compression system.

(ii) *The pressure balance* was that used by Scott. As it was deemed inadvisable to load it to pressures above 600 atmospheres the pressure range covered in the present investigation is limited to this figure, although a new balance for work up to 1500 atmospheres has been acquired from Messrs. Budenberg & Co. and recently brought into use.

(iii) *The glass measuring system* (fig. 2, H) was reconstructed in order to cope with the greater volumes of released gas measured as higher pressures were employed. At the same time various minor improvements in design were effected.

Procedure.—In all essentials the experimental procedure was that previously adopted except that for determinations at 0° C. the high pressure vessel was immersed in a separate and specially constructed ice-water bath, the large water bath maintained at 25° C. being then used for the measurement of released gas only.

Preparation of Gases.—The hydrogen and carbon monoxide were from the same sources as before; chemical analyses showed their purities to be 99·9 and 99·8 per cent. respectively. Both the single gases and the gas mixtures were prepared in quantities of 100 cubic feet and subsequently compressed into special cylinders capable of withstanding 400 atmospheres pressure; these each in turn formed the first unit in the filling system of the compressibility apparatus. The composition of the gases used was checked by chemical analysis both before and after compression and after release from the high pressure vessel.

It should be added that (i) the activated cocoanut shell charcoal contained in the steel tube D (fig. 2) was found to be quite efficient in removing any iron carbonyl possibly present in the compressed gases; this could be shown by the absence of iron lines in spectrograms of flames of the released gases burning in air at the exit tube of the apparatus, and (ii) there was never any evidence of the reaction $2CO \rightarrow C + CO_2$ having proceeded under our experimental conditions; for example, on passing 10 cubic feet of carbon monoxide which had been stored under pressure in one of the cylinders used in this investigation for 6 months, through a solution of baryta, the precipitated barium carbonate indicated merely 0·06 per cent. of CO_2 in the original gas.

Results.

Values of pv_A which have been taken from smooth isotherms (fig. 3) at suitable pressure intervals are given in Tables I and II. They are expressed in the usual form $pv_A = PV/P_0V_0$ where PV is the pressure-volume product of a given mass of gas under the experimental conditions and P_0V_0 this value for

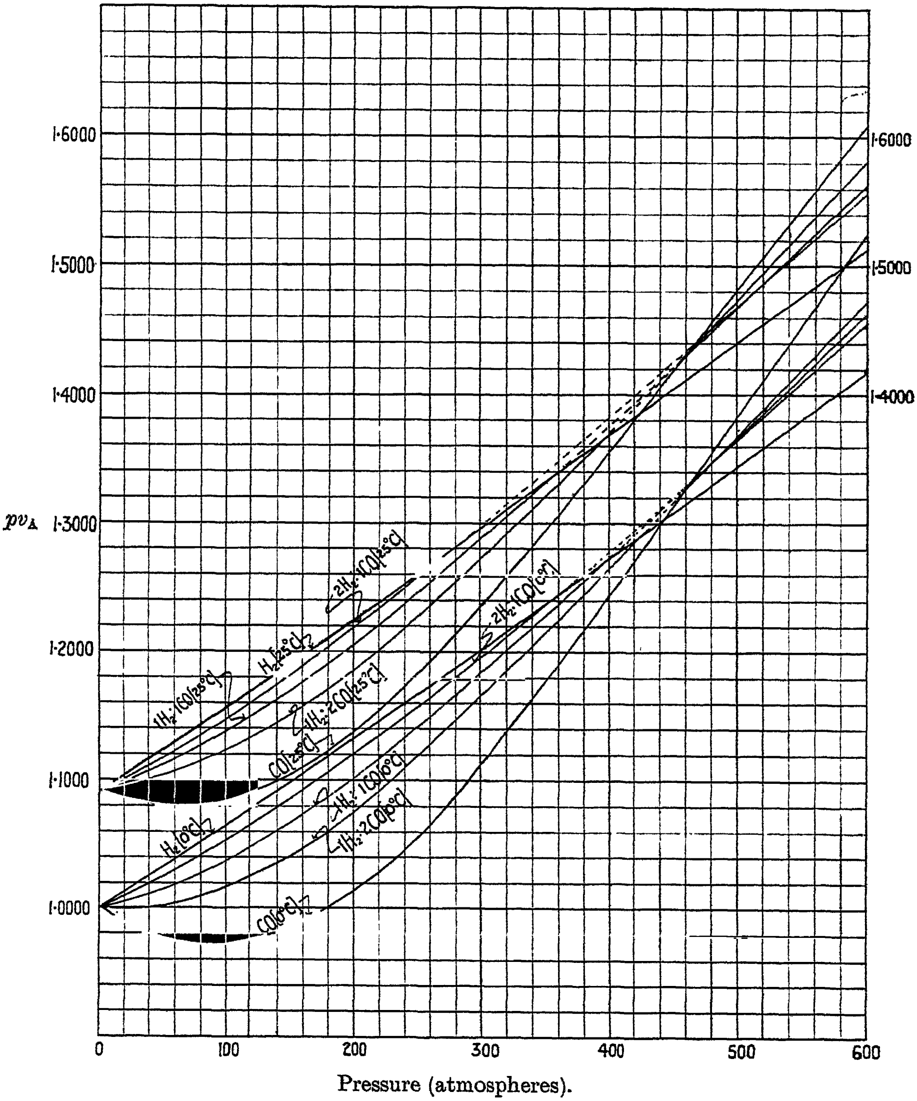

FIG. 3.—Isotherms at 0° and 25° C.

the same mass of gas at N.T.P.* In calculating these values the coefficient of expansion at atmospheric pressure both for the single gases and gaseous mixtures has been taken as 0·003662. Also, at pressures above 200 to 250 atmospheres, we have applied a small correction for the change in volume of the high pressure vessel with increase in total pressure. In making this correction we have followed Bartlett in applying Love's formula† and calculation by means of it shows a probable change in volume of 0·08 per cent. at 600 atmospheres pressure.

The isotherms are best represented in the usual manner by equations of the form

$$pv_A = a + bp + cp^2 + dp^3,$$

where a, b, c and d are constants. The values of these constants determined from the figures in Tables I and II are given in Table III; pv_A values calculated therefrom are usually in close agreement with the observed data.

Table I.—pv_A-values at 0° C.

P.	H_2.	66·6H_2 : 33·4CO.	50·2H_2 : 49·8CO.	33·3H_2 : 66·7CO.	CO.
atmos.					
1	1·0000	1·0000	1·0000	1·0000	1·0000
10	1·0058	1·0043	1·0022	0·9995	0·9938
20	1·0124	1·0094	1·0050	0·9992	0·9880
40	1·0255	1·0196	1·0114	1·0005	0·9786
60	1·0386	1·0304	1·0193	1·0038	0·9728
80	1·0520	1·0418	1·0275	1·0091	0·9703
100	1·0654	1·0540	1·0377	1·0165	0·9710
120	1·0789	1·0659	1·0486	1·0248	0·9745
140	1·0922	1·0790	1·0608	1·0352	0·9811
160	1·1060	1·0918	1·0733	1·0468	0·9900
180	1·1196	1·1055	1·0870	1·0602	1·0013
200	1·1332	1·1195	1·1016	1·0747	1·0152
250	1·1677	1·1562	1·1406	1·1152	1·0586
300	1·2025	1·1954	1·1829	1·1618	1·1126
350	1·2377	1·2360	1·2280	1·2121	1·1745
400	1·2732	1·2781	1·2743	1·2644	1·2423
450	1·3091	1·3214	1·3213	1·3177	1·3128
500	1·3450	1·3657	1·3675	1·3699	1·3840
550	1·3816	1·4102	1·4142	1·4209	1·4532
600	1·4183	1·4550	1·4620	1·4725	1·5242

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* The direct calculation of the pv_A values from the experimental figures is made by means of the expression $pv_A = (1 + \alpha t) P_2V_2/P_1V_1$, where pv_A is the pressure volume product at P_2 atmospheres pressure and t° C., V_2 the volume of the high pressure vessel and V_1 the total volume of the gas upon expansion and measured at atmospheric pressure P_1.

† Love, "Mathematical Theory of Elasticity," p. 14, Cambridge Univ. Press (1920).

Table II.—pv_A-values at 25° C.

P.	H_2.	$66 \cdot 6H_2 : 33 \cdot 4CO$.	$50 \cdot 2H_2 : 49 \cdot 8CO$.	$33 \cdot 3H_2 : 66 \cdot 7CO$.	CO.
atmos.					
1	1·0915	1·0915	1·0915	1·0915	1·0915
10	1·0972	1·0957	1·0945	1·0926	1·0877
20	1·1034	1·1012	1·0984	1·0950	1·0846
40	1·1162	1·1120	1·1068	1·1002	1·0806
60	1·1292	1·1235	1·1164	1·1069	1·0792
80	1·1423	1·1354	1·1268	1·1146	1·0807
100	1·1556	1·1480	1·1376	1·1239	1·0838
120	1·1691	1·1609	1·1494	1·1346	1·0905
140	1·1827	1·1746	1·1623	1·1462	1·0992
160	1·1965	1·1885	1·1759	1·1589	1·1100
180	1·2105	1·2029	1·1900	1·1727	1·1230
200	1·2245	1·2176	1·2049	1·1875	1·1382
250	1·2600	1·2563	1·2444	1·2278	1·1820
300	1·2960	1·2968	1·2866	1·2729	1·2344
350	1·3320	1·3388	1·3308	1·3214	1·2933
400	1·3686	1·3820	1·3767	1·3725	1·3565
450	1·4049	1·4255	1·4235	1·4250	1·4239
500	1·4411	1·4694	1·4701	1·4773	1·4908
550	1·4767	1·5129	1·5159	1·5298	1·5580
600	1·5128	1·5560	1·5622	1·5825	1·6252

Table III.—$pv_A = a + bp + cp^2 + dp^3$.

At 0° C.	a.	$b \times 10^3$.	$c \times 10^6$.	$d \times 10^9$.
$100H_2$	0·999347	0·65267	0·09192	−0·0285
$66 \cdot 6H_2 : 33 \cdot 4CO$	0·999524	0·47706	0·69268	−0·3623
$50 \cdot 2H_2 : 49 \cdot 8CO$	0·999772	0·22506	1·68232	−1·3228
$33 \cdot 3H_2 : 66 \cdot 7CO$	1·000093	−0·092673	2·75855	−2·1882
100CO	1·000729	−0·73386	4·72196	−3·4452

At 25° C.	a.	$b \times 10^3$.	$c \times 10^6$.	$d \times 10^9$.
$100H_2$	1·090905	0·62183	0·27938	−0·2454
$66 \cdot 6H_2 : 33 \cdot 4CO$	1·090912	0·49548	0·80649	−0·5677
$50 \cdot 2H_2 : 49 \cdot 8CO$	1·090986	0·34521	1·31263	−0·9741
$33 \cdot 3H_2 \cdot 66 \cdot 7CO$	1·091193	0·14876	1·93103	−1·3644
100CO	1·091825	−0·44569	3·98143	−2·9657

When plotted against mixture composition (fig. 4) the values of b, c and d are seen to lie on fairly smooth curves, and with their aid it is possible approximately to derive the equation of the isotherm of any hydrogen-carbon monoxide mixture at either 0° or 25° C.

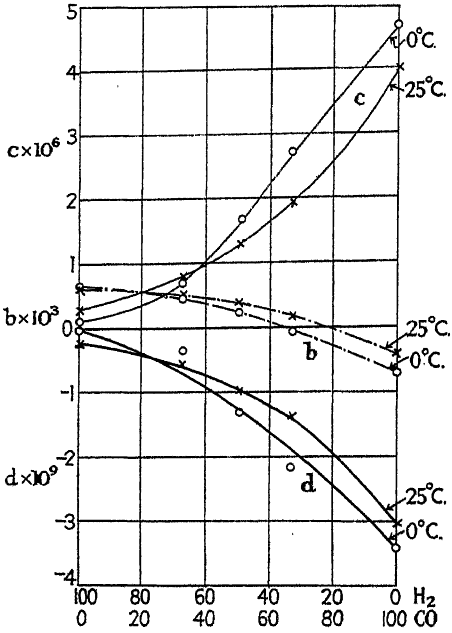

FIG. 4.

Discussion of Results.

It is now well appreciated that the laws of " additive volume " and " additive pressure " do not hold at high pressures. It may be of interest to note, however, that calculations based on the " additive volume " law show the observed volumes occupied by the gaseous mixtures to be generally greater than the sum of the volumes occupied by the single gases separately at the same pressure (a result indicated by the isotherms of the mixtures lying nearer to the hydrogen isotherm than would occur if a linear relationship with composition held good), the greatest deviation being 2·5 per cent. in the case of the H_2 : CO mixture at 0° C. and at approximately 205 atmospheres pressure. The deviations of all three mixtures reach a maximum, which at 0° C. occurs at about 200 atmospheres pressure, and afterwards decrease in magnitude and may become negative at pressures higher than 500 to 600 atmospheres. Also, the deviations are found to be greater at 0° than at 25° C. and in this connection it may be recalled that Bartlett* when studying the compressibility of hydrogen, nitrogen and a 3 : 1 mixture of the two showed that at temperatures above 300° C. the additive volume law holds good.

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* 'J. Amer. Chem. Soc.,' vol. 50, p. 1275 (1928).

The additive pressure law does not hold good even approximately. For example, in the case of the $H_2 : CO$ mixture at 600 atmospheres pressure a deviation of about 25 per cent. occurs. Recently Bartlett has attempted to correlate the pressure exerted by a mixture with its composition by the following modification of the "additive pressure" law: "At constant temperature the pressure exerted by one constituent in a gaseous mixture equals the product of its mol fraction, and the pressure it would exert as a pure gas at a molecular concentration equal to the molecular concentration of the mixture." The deviations from this version of the law when applied to the data recorded herein never exceed 2 per cent., which show it to be a useful approximation.

No attempt has been made to apply any one of the recently proposed equations of state to our results on account of the limited temperature range so far covered; nor has any application been made of the Lennard-Jones partial pressure law which correlates the values of "b" in the equations $pv_A = a + bp +$ etc., for isotherms of gaseous mixtures because it affords little help at high pressures where the "c" and "d" terms may preponderate.

Recently Lennard-Jones* has pointed out the possibility of greater deviations from Boyle's law being exhibited by certain gaseous mixtures than by either of the separate constituents. This is attributed to the fact that the temperature of maximum deviation of a gaseous mixture lies between those of its constituents and striking confirmation of the effect has been forthcoming as the result of researches by Masson and his collaborators† into the compressibility of hydrogen-helium and hydrogen-argon mixtures at pressures up to 125 atmospheres. A not unlike phenomenon may be observed on studying the isotherms in fig. 3 where, at 0° C. between pressures of about 370 to 460 atmospheres (dotted lines) and at 25° C. between about 290 to 460 atmospheres, the three hydrogen-carbon monoxide mixtures studied are less compressible than either hydrogen or carbon monoxide taken singly. It would not appear that these results call for any new explanation; no doubt they are special cases of the deviations already well recognised.

Reference to Bartlett's isotherms (*loc. cit.*)‡ for a $3H_2 : 1N_2$ mixture reveals a similar feature; indeed, as indicated by Scott, the behaviour of hydrogen-carbon monoxide mixtures follows closely that of hydrogen-nitrogen mixtures.

The investigation is being extended to cover a pressure range up to 1000 atmospheres at temperatures up to 300° C.

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* 'Nature,' vol. 119, p. 459 (1927); 'Proc. Roy. Soc.,' A, vol. 115, p. 334 (1927).

† 'Proc. Roy. Soc.,' A, vol. 122, p. 283 (1929); vol. 126, p. 268 (1930).

‡ See also 'J. Amer. Chem. Soc.,' vol. 49, p. 687 (1927).

Summary.

The isotherms of hydrogen, carbon monoxide and three mixtures of these gases containing 66·6, 50·2 and 33·3 per cent. of hydrogen respectively have been determined over a pressure range extending to 600 atmospheres at both 0° C. and 25° C.

Each isotherm has been expressed in the form $pv_A = a + bp + cp^2 + dp^3$, and the values of a, b, c and d tabulated in each case. The isotherms of the mixtures, which are similar to those of hydrogen and nitrogen, show that over certain pressure ranges extending from about 300 to 470 atmospheres the mixtures are less compressible than either of the constituent gases.

The Kinetics of Adsorption Processes.

By A. R. UBBELOHDE, B.A., B.Sc., and A. EGERTON, F.R.S.

(Received October 2, 1931.)

Introduction.

In any process of adsorption, dynamic equilibrium is reached when the number of molecules condensing in unit time on the adsorbing surface is equal to the molecules evaporating. Langmuir* obtained the well-known relation between the mass adsorbed and the pressure

$$m = k_1p/(k_2p + b)$$

by writing the number of molecules evaporating as proportional to the number already adsorbed, and the number condensing as equal to na_0kp, where p is the pressure, n the fraction of the adsorbing space unoccupied, k a constant derived from the kinetic theory of gases, and a_0 an accommodation coefficient, which was supposed to differ very little from unity. Using these assumptions, adsorption equilibria should be reached so rapidly as to be practically instantaneous.

If we regard the process of adsorption as analogous to a chemical reaction, involving changes in behaviour of the valency electrons of the adsorbed molecules and the adsorbent, the assumption that a_0 differs little from unity, corresponds with the assumption that every collision is fruitful in a gas reaction. H. S. Taylor* has pointed out in a recent paper that for some adsorption processes it is apparently necessary to assume quite large energies of activation. Instead of all the molecules colliding with " unoccupied " spaces being adsorbed, only a fraction $e^{-E/RT}$ of the impinging molecules change over into adsorbed molecules.

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* I. Langmuir, ' J. A. C. S.,' vol. 40, p. 1361 (1918).

Adsorption equilibria involving a large energy of activation would be reached fairly slowly, and Taylor quotes a number of cases which might be explained in this way. Many adsorbents, however, are finely divided solids with distorted lattices, and the possibility of a slow diffusion of adsorbed substance into the solid cannot always be neglected as an alternative explanation of slow adsorption equilibria.†

Allmand and others‡ have shown that adsorption isothermals are not necessarily continuous, and that it is necessary to determine a large number of equilibrium points in order to obtain the exact shape. This peculiarity may be closely connected with the kinetics of the adsorption process.

The experimental method of studying the kinetics of adsorption processes to be described in this paper is simple, and has the further advantage of furnishing the fine detail of adsorption isothermals without undue labour.

The system studied—the adsorption of hydrogen on charcoal at the boiling point of liquid oxygen—happened to be chosen because of its relation with another research, which it is hoped to publish soon. Charcoal at these temperatures catalyses the attainment of equilibrium between ortho and para hydrogen.§ G. v. Elbe and F. Simon|| have shown, by measurements of the heat evolved, that at the temperature of liquid N_2 little further change in the relative amounts of the two rotational isomers takes place after 6 minutes in contact with the charcoal, whereas at the temperature of liquid hydrogen some 25 minutes are required. If it is assumed that the rate of change is proportional to the amount present, this gives 2000 cals. as a very rough estimate of the energy of activation in presence of the catalyst. A. Farkas,¶ measuring the rate of reaction in the gas phase at high temperatures, mentions an energy of activation of the order of 4200 cals. for the homogeneous reaction.

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* H. S. Taylor, 'J. A. C. S.,' vol. 53, p. 578 (1931).

† J. W. MacBain, 'Phil. Mag.,' vol. 18, p. 916 (1909).

‡ A. J. Allmand and L. J. Burrage, 'Proc. Roy. Soc.,' A, vol. 130, p. 610 (1931).

§ K. Bonhoeffer and P. Harteck, 'Z. Phys. Chem.,' B, vol. 4, p. 113 (1929).

|| G. v Elbe and F. Simon, 'Z. Phys. Chem.,' B, vol. 6, p. 79 (1929).

¶ A. Farkas, 'Z. Phys. Chem.,' B, vol. 10, p. 419 (1930).

The Dynamic Method of Determining Isothermals.

Starting with a system in equilibrium, and removing gas from it continuously, the pressure in the system at any moment will only be equal to the equilibrium pressure for the same amount of gas removed if adsorption and evaporation equilibria are instantaneous. If equilibrium takes time, either because an activation process is necessary, or for other reasons, the pressure at any moment will be lower than the equilibrium pressure on the removal isothermal, and higher on the additional isothermal.

The mass of gas removed in unit time is controlled by connecting the system with a steel mercury pump of high velocity through a capillary, the length and diameter of which can be varied. The resistance of all connecting tubes of the apparatus is negligible compared with that of the capillaries used. Since the pressure at one end of the capillary is the pressure P of the system, and the pressure at the other end is zero, the mass of gas flowing out in unit time is $k\mathrm{P}^2$, according to Poiseuille's law. k is a constant depending on the diameter and length of the capillary, and on the viscosity and temperature of the gas flowing through it; it is determined directly by measuring the mass of gas flowing through the capillary at various pressures, so that Poiseuille's law need not be assumed.

By plotting the mass of gas against the pressure, what may be called a dynamic isothermal will be obtained. This can be repeated with a series of capillaries of increasing resistance. As the rate of removal of gas decreases, more time is given for equilibrium, and the dynamic isothermal approximates more and more closely to the static isothermal. This may, if necessary, be determined by extrapolation. By studying the lag between the static and dynamic isothermals, the time required for adsorption equilibrium can be determined, and it can be seen whether this varies over different parts of the static isothermal.

Experimental Procedure.

Fig. 1 gives a diagrammatic representation of the apparatus. 1·95 grams of nut charcoal activated by steam was contained in a thin glass bulb immersed in liquid oxygen, and was connected, by way of a liquid-air trap to keep out mercury vapour, to a mercury manometer, and to a capillary tube. Before use the charcoal was baked out *in vacuo* in a sulphur bath for about 2 hours, then placed in contact with pure hydrogen at the temperature of liquid oxygen, then baked out again. The baking and washing out with hydrogen were repeated three times, in order to remove any gases from the system that could only be displaced by adsorbed hydrogen (*cf.* Allmand and Burrage). Pure hydrogen was then introduced into the charcoal bulb till the equilibrium pressure was about 25 cm., and the system was left for 30 minutes or more, in order to allow the rotational isomers to come to equilibrium.

At this stage the tap connecting the system to the capillary was opened, and alternate columns of the manometer were read every half-minute with a cathetometer, reading to 0·001 cm. till the pressure of gas over the charcoal had decreased to about 7 cm. From these readings a curve can be constructed showing the pressure over the system at any time.

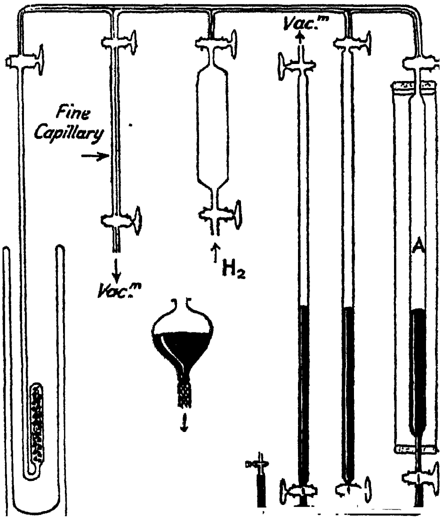

Fig. 1.

The mercury columns of the manometer, as well as the rest of the apparatus, were mounted in a room of very constant temperature, and free from vibration. The columns were of about 1 cm. internal diameter. At the rates of change of pressure actually used the effect of the inertia of the columns on the instantaneous difference in levels is quite negligible. The other possible source of error in using a mercury manometer for measuring changes of pressure is due to a difference in the capillarity correction in the two columns. This difference arises from a difference in contact angles. Sticktion is mainly due to the difference between the advancing and receding contact angles of mercury on glass. Actually the receding meniscus is seen to be flatter than the advancing one. We may assume with Adam and Jessop* that the frictional force F (which is the same as the difference of pressure due to sticktion) is $\pi R\gamma$ (cos a — cos r), where a and r are the advancing and receding contact angles. Writing γ, the surface tension of mercury, as 547 dynes/cm., the radius R of the tube as 0·5 cm., a as 140° and r as roughly 110°, the maximum value of F becomes 0·01 cm. Hg. This difference remains constant provided the two angles do not change, so that sticktion introduces a difference of pressure that is constant as long as the two columns are in motion on clean glass. Its effect on the values of P and $d\mathrm{P}/dt$ will therefore be very small. Other possible reasons for difference in contact angle are local irregularities in the nature of the surface and electrification. These differences, which would not lead to a correction of more than 0·01 cm., were avoided by using different portions of the manometer in the several experiments. Blank experiments have been made to evaluate these errors at the rates of change of pressure actually used.

The hydrogen was prepared by the electrolysis of KOH saturated with baryta; an all-Pyrex glass generator specially designed for making fairly large quantities of pure H_2 was used. The gas was passed over a drying agent, then over a long platinum coil, inserted between concentric silica tubes to secure intimate contact, and heated electrically to remove traces of oxygen. Finally the hydrogen was passed over a long (60 cm.) inclined P_2O_5 tube into a reservoir bulb. The P_2O_5 was washed with hydrogen and evacuated before use.

The purity of the hydrogen used in these experiments was tested by comparing its thermal conductivity at 25·3° C. with that of hydrogen obtained by diffusion through a large hot Pd tube. The thermal conductivity of the residual hydrogen which is allowed to evaporate from the charcoal, on removal of the liquid oxygen bath, was also measured; impurity in the original supply would probably be retained preferentially by the charcoal when cooled, and the accumulated impurities after two or three experiments would show up to an increasing extent in the gauge used for measuring the thermal conductivities. Tests with mixtures of nitrogen and hydrogen showed that an impurity of 0·04 per cent. in the hydrogen would be definitely noticeable; possible impurities in the hydrogen used were shown not to be bigger than this.

Calibration of the Capillaries.

The capillaries were calibrated for mass flowing out in unit time at different pressures by connecting them with a burette A, of known volume, containing hydrogen, and measuring the pressure of the system at intervals. The mass of gas flowing out in unit time was found proportional to the square of the pressure, in accordance with Poiseuille's formula.

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* N. K. Adam and G. Jessop, 'J. C. S.,' p. 1865 (1925).

The hydrogen used in this calibration contains the equilibrium 75 per cent. ortho H_2, whereas that flowing through the capillaries is the equilibrium mixture at the temperature of liquid oxygen, and contains 50 per cent. ortho H_2. If the capillaries are used to measure the mass flowing out it is necessary to show that the two mixtures have the same viscosity. Careful comparisons made at constant temperature by the Rankine method indicated that the difference between the two viscosities at a temperature about 15° C. was not more than 0·3 per cent. The higher viscosity is shown by the 50 per cent. mixture. This result is not likely to be due to impurities, but is at the limit of accuracy of the experiments. Any reversion which occurs by catalysis in the capillary would make the real difference greater.

The accuracy of timing the rate of fall is being increased, and if the result is confirmed it would throw an interesting light on the transfer of energy by the two rotational isomers. As such a difference is very small it would only introduce a small correction factor in the estimates of the mass removed, and it is neglected in the data given in this paper.

Temperature of the Charcoal.

The charcoal bulb was immersed in liquid oxygen, supplied by the British Oxygen Company and allowed to stand a day or two before use. On account of evaporation the surface of liquid oxygen fluctuates considerably in temperature, so that the bulb was always kept at least 5 cm. below the surface. The temperature of the bath was calculated from the barometric pressure, using the formula $t = 183 \cdot 00 + 0 \cdot 0126 \ (p - 760)$. Constancy was tested by a five-junction copper-constantan couple.

The heat of adsorption or of evaporation of the gas will alter the temperature of the adsorbent slightly in the dynamic method, increasing the lag both of the addition and removal isothermals. In the present experiments the fastest rates of removal actually used led to a loss of about 0·1 cal./minute from the system. If there were no equalisation of temperature, this might lead to a temperature difference of about a degree. The lag from this cause is thus not likely to be large.

Calculation of the Results.

When the tap is opened to the capillary the levels of the mercury columns of the manometer are read every alternate half-minute, *i.e.*, each column is read once every minute. By interpolation the position of each column, and hence the pressure of the system, is calculated for each half-minute from the start. From these figures two results can be obtained.

(*a*) *The Slope of the Dynamic Isothermal.*—Neglecting the lag for the moment, the pressure P of the system is a function of the mass m present,

$$\mathrm{P} = f(m) \quad \text{and} \quad \frac{\partial \mathrm{P}}{\partial t} = f'(m)\,\frac{\partial m}{\partial t},$$

but $\partial m/\partial t = k\mathrm{P}^2$, where k depends on the capillary used. Hence

$$\frac{\partial \mathrm{P}}{\partial t} = k\mathrm{P}^2 f'(m),$$

where $f'(m)$ is the slope of the dynamic isothermal.

Since the pressure P at each half-minute is known, the values of $\partial \mathrm{P}/\partial t$ can easily be found. The slope of the isothermal is proportional to this. Plots of

$$\frac{1}{k\mathrm{P}^2}\,\frac{\partial \mathrm{P}}{\partial t}$$

against P show up any change of slope, such as the discontinuities described by Allmand.

(*b*) *The Dynamic Isothermal.*—Starting with a known mass of gas in the system, and leaving it to come to an equilibrium pressure P_0 before opening the tap, the mass of gas removed during any interval $(t_1 - t_2)$ after the tap is opened will be

$$\Delta m = \int_{t_1}^{t_2} k\mathrm{P}^2 dt.$$

A sufficient approximation to this integral is obtained as follows :—

Treating $d\mathrm{P}/dt$ as constant $(= \Delta\mathrm{P})$ over each minute, Δm during that minute will be given by

$$\frac{1}{\Delta \mathrm{P}} \int_{\mathrm{P}_1}^{\mathrm{P}_2} k\mathrm{P}^2\, d\mathrm{P} = \Delta m.$$

But over the interval of 1 minute $(\mathrm{P}_2 - \mathrm{P}_1) = \Delta\mathrm{P}$; thus

$$\Delta m = \frac{k}{3\,\Delta\mathrm{P}}(\mathrm{P}_2{}^3 - \mathrm{P}_1{}^3) = k/3\,(\mathrm{P}_1{}^2 + \mathrm{P}_1\mathrm{P}_2 + \mathrm{P}_2{}^2).$$

Neglecting terms in $(\Delta\mathrm{P})^2$ this reduces to

$$\Delta m = k\,(\mathrm{P}_1{}^2 - \mathrm{P}\,\Delta\mathrm{P}),$$

where P_1 is the pressure at the beginning of the interval considered.

From tables showing the value of P each minute the mass removed during the minute is calculated, using the above approximation. The total mass removed at any time is found by summation. The initial mass of gas present in the system is found by direct measurement, or from an addition dynamic isothermal in which the system is originally completely evacuated. The initial mass less the mass removed, *i.e.*, the mass still present, is plotted against the pressure to give the dynamic isothermal.

Experimental Results.

After a number of preliminary experiments three different lengths of the same capillary tubing were selected, of radius approximately 2×10^{-2} cm. The constant k in Poiseuille's equation is determined as explained; when the temperature of the calibration is different from the temperature at the time of the experiments a small correction is applied, to allow for the change in viscosity of the hydrogen with temperature.

Cap. I.—$k_1 = 0{\cdot}344 \pm 0{\cdot}005$ (mean of 12 readings). Temperature of oxygen bath = − 183·09° C. Temperature of capillary 16·63° C.

Cap. II.—$k_2 = 1{\cdot}381 \pm 0{\cdot}007$. Temperature of oxygen bath = − 183·19° C. Temperature of capillary 18·47° C.

Cap. III.—$k_3 = 1{\cdot}241 \pm 0{\cdot}02$. The liquid oxygen used was a fresh arrival, and the bath temperature was abnormally low owing to the presence of nitrogen in the liquid oxygen. Temperature of capillary 17·1° C. On account of the larger error of calibration, the results with this capillary have not been used for calculation of the isothermal. k is expressed in cubic centimetres and centimetres of mercury as units.

A plot of $d\text{P}/dt$ against P for a given capillary gives closely similar curves for the different sets of readings, showing that the slope of the dynamic isothermal is reproducible under the experimental conditions after the initial three or four points. From plots of each set the slope at corresponding pressures is estimated and the mean is taken. The total number of corresponding pressures chosen is about the same as the number of experimental readings.

In the fig. 2 the actual isothermals are plotted for capillaries I and II; the data for this are calculated from the sets of readings of P and t, as explained on p. 517. The two isothermals differ very little in slope. In the same figure the above values of $d\text{P}/kdt$ are plotted against the pressure. The slopes are seen to be initially about the same; at lower pressures the slope for capillary II (which gives the faster removal of gas) is on the average about 5 per cent.

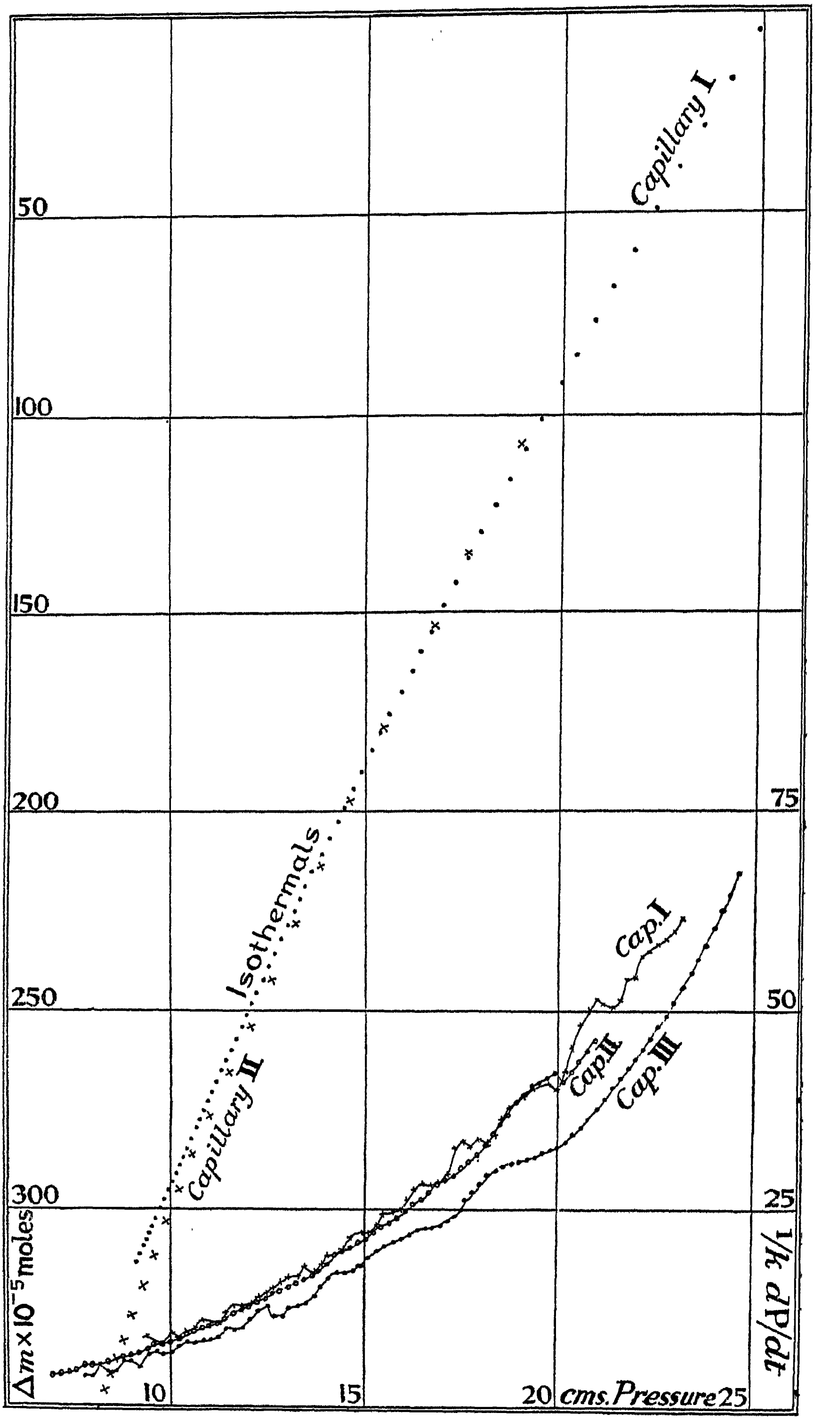
50
100
150
200
250
300
Δm×10⁻⁵ moles
10
15
20
cms. Pressure 25
75
50
25
1/k dP/dt
Capillary I
Isothermals
Capillary II
Cap. I
Cap. II
Cap. III

FIG. 2.

less than that for capillary I. Since the removal of hydrogen in the dynamic isothermal is irreversible in the thermodynamic sense, more work will be required to bring it to a standard state, *i.e.*, the dynamic isothermal will show lower pressures than the static isothermal. The experiments quoted agree with this. The measurements made with capillary II refer to a slightly lower temperature, which would necessarily give an isothermal of lesser slope. Thus increasing the rate of removal fourfold makes less than 5 per cent. difference to the slope, and desorption equilibrium is certainly very rapid in the case of hydrogen on charcoal at these temperatures.

If q is the heat of adsorption per gram molecule for a system containing a constant mass of hydrogen, $d\ln P/dT = -q/RT^2$. Treating q as independent of temperature, $p = Ae^{-q/RT}$, where A is a constant. If E is the energy of activation necessary for adsorption, the rate of condensation or of evaporation at equilibrium is

$$kpe^{-E/RT} = Be^{-(q+E)/RT},$$

where B is a constant. In order to determine the actual value of the activation energy it is therefore necessary to carry out experiments at a number of temperatures. The system charcoal/hydrogen is not very suitable for this, so that experiments of the same kind are being continued with palladium and hydrogen.

Inspection of the data and of fig. 2 shows that the slope of these isothermals is apparently not a continuous function of the pressure. The curve for capillary II reproduces several of the features of curve I, although it is smoother on account of the smaller number of points which can be observed at the bigger rate of removal of hydrogen. A plot of the readings for capillary III is also given, since errors in k make no important difference to the shape of the curve; it again shows discontinuities.

The probable error in the data quoted has been estimated, both from the fluctuations of the different experimental values about the mean and from experiments made on hydrogen streaming out under identical conditions, but in the absence of charcoal. Certain discontinuities, such as those on the regions of 16·5 and 14·5 cm., which persist in the various experiments, are larger than the error so determined, though admittedly they are on the limit of what can be detected with the present precision. The fluctuations from the mean in the several sets of observations give a measure of the effect of such errors, and in the regions quoted they are within ± 0·003 cm., which is insufficient to account for the discontinuity observed. The plots of

$$\frac{1}{kp^2}\frac{dp}{dt}$$

of course show similar discontinuities. These discontinuities may perhaps be compared with those observed by Allmand and others, though they obtained their results with vapours at room temperatures, and with pressures below 1 cm. of mercury. The exact specific surface of charcoal is not known, but rough calculation shows that the breaks are too frequent to be due to successive layers of adsorbed gas. The adsorbed molecules are held partly by forces due to the charcoal, and partly by their attraction for one another. It may be assumed that the charcoal surface is made up of regions of different adsorption potential, but there is no *a priori* reason to suppose that these regions are not distributed smoothly about a mean value, so as to give rise to discontinuities. It seems more plausible to ascribe these to the lateral attraction between the molecules reaching critical values ; in the case of the adsorption of vapours on charcoal it has been supposed (Allmand and Burrage) that a sort of liquefaction takes place. In the present case the system is well above the critical temperature of hydrogen, so that another explanation must be found. It is suggested that the relation between the rotational state of the molecule and the adsorption potential may furnish an explanation. In the case of hydrogen and charcoal we must assume large adsorption potentials in order to explain the extent to which adsorption takes place even at relatively high temperatures. Only exceptionally activated molecules will be free to move from one point on the adsorption network to another. The molecules anchored to fixed points may still be free to rotate, however ; if it is supposed that the polarisability of the hydrogen molecule is different along the axis joining the atoms and that at right angles, there will be a sudden decrease both in the adsorption potential and in the lateral attraction when the molecules begin to rotate. (A similar problem has been discussed for crystals.*) The change will be bigger for adsorbed than for liquid hydrogen, on account of the greater deformation of the molecules.

The result obtained by T. Stern† for crystals may be applied to the adsorbed molecules ; these will rotate, or will oscillate about a mean position, according as

$$W \gtrless 2V_0,$$

where W is the rotational energy, and V_0 the function expressing the change of potential energy with orientation. Even if the adsorption potential for non-rotating molecules decreases smoothly from high to low values in the different regions, there will be a number of critical points at which molecules possessing n_1 $(n - 1), \ldots$, 2 and 1 quanta of rotation just begin to rotate. The position of these points on the isothermal depends both on W and on V_0. For very symmetrical molecules, such as CCl_4, V_0 will be small, and discontinuities may be expected even at low pressures. There should, however, be a pressure on all isothermals above which no further discontinuities occur. In the present case this might be about 22 cms. of mercury, but a careful inspection of the isothermal over bigger ranges of pressures and with higher precision is needed to decide these points.

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* L. Pauling, 'Phys. Rev.,' vol. 36, p. 431 (1930).

† T. E. Stern, 'Proc. Roy. Soc.,' A, vol. 130, p. 551 (1931).

If this explanation be correct, ortho and para hydrogen should show different absorbabilities in the regions of pressure considered. It is hoped to publish an account of some experiments which have been made to test this point. In conclusion, it may be pointed out that the molecules adsorbed on the most active points in heterogeneous catalysis will not in general be rotating, and low values of activation energy may be connected with this fact.

Summary.

A method is described for studying the adsorption isothermal in great detail, using different rates of removal of the sorbate. Data are quoted for the adsorption of hydrogen on charcoal at the temperature of liquid oxygen. The rate of establishment of equilibrium on desorption is very rapid. The possible influence of the rotational state of the adsorbed molecules on the adsorption potential, and on the discontinuities in the isotherm, is also discussed. The difference in viscosity of a 75 per cent. mixture of ortho and para hydrogen, and of a 50 per cent. mixture, is shown to be less than 0·3 per cent.

On the Mass of the Proton.

By Sir Arthur Eddington, F.R.S.

(Received November 3, 1931.)

1. This paper develops, and to some extent amends, the theory of the relation of the proton to the electron suggested in a " Preliminary Note on the Masses of the Electron, the Proton, and the Universe."* As explained in that note, my discussion of the constant 137 opened out into a wider investigation embracing other natural constants, and it seemed necessary to pursue this before attempting to perfect the theory of 137.

The first result of this extension is contained in a paper on " The Value of the Cosmical Constant."† This is primarily a theory of the mass of an electron; it is satisfactorily confirmed by the observed velocities of recession of the spiral nebulæ, and I think it must be substantially true. But the acceptance of this theory of the electron has the consequence that the relation between the electron and the proton cannot come about quite in the way I had previously had in mind. Indeed, my first impression was that it closed the door to any symmetrical kind of relation between the electron and proton. For my own part, I think it most unlikely that there is any fundamental difference in the intrinsic nature of protons and electrons, and I should regard it as a serious objection to the theory of the cosmical constant if it insisted on such a difference. It is therefore important to show that there is an opening by which the proton is easily brought into the same scheme.

The difficulty, as it first appeared, may be stated as follows. According to the theory of the cosmical constant, we can calculate from the observed recession of remote objects (spiral nebulæ) the mass-term occurring in the fundamental wave equation. The mass turns out to be the mass of an electron. Why an electron rather than a proton ? The theory employed is purely geometrical, so that it is difficult to see how it can acquire a bias towards one kind of charge unless the relation of an electron to space-time is actually of a simpler kind than that of a proton. The intention of the present paper is to answer the question by showing that a reasonable development of the geometrical theory enables us to calculate the mass of the proton as well as that of the electron from the recession of the spiral nebulæ in a way which removes all suggestion of bias towards the electron. It appears that the mass-term originally calculated was strictly $Mm/(M+m)$, which is symmetrical with respect to the proton and electron, though it is almost indistinguishable from the mass m of the electron.

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* 'Proc. Camb. Phil. Soc.,' vol. 27, p. 15 (1931).

† 'Proc. Roy. Soc.,' A, vol. 133, p. 605 (1931). I regret that there is an error in the brief " digression " on the proton on p. 613. In the second equation in (12) the coefficient 10 is incorrect and this renders the digression pointless.

2. Dirac's equation for a single electron, written in my usual notation, is

$$\left\{\frac{ih}{2\pi}\left(E_1\frac{\partial}{\partial x_1}+E_2\frac{\partial}{\partial x_2}+E_3\frac{\partial}{\partial x_3}+E_4\frac{\partial}{\partial x_4}\right)+mc\right\}\psi=0, \tag{2.1}$$

where E_1, E_2, E_3, E_4 are anticommuting square roots of -1, so that

$$E_\mu{}^2=-1 \qquad E_\mu E_\nu+E_\nu E_\mu=0. \tag{2.2}$$

Consider an elementary solution consisting of plane waves in the direction

$$s=l_1x_1+l_2x_2+l_3x_3+l_4x_4,$$

l_1, l_2, l_3, l_4 being direction cosines. Let

$$E_s=l_1E_1+l_2E_2+l_3E_3+l_4E_4,$$

so that by (2.2)

$$E_s{}^2=-1. \tag{2.3}$$

Then (2.1) reduces to

$$\left(iE_s\frac{\partial}{\partial s}+\frac{2\pi mc}{h}\right)\psi=0. \tag{2.4}$$

According to the theory of the cosmical constant (*loc. cit.*, § 8, equation (12))

$$\frac{2\pi mc\alpha}{h}=\frac{\sqrt{N}}{R},$$

where α is the fine structure constant 137, N the total number of electrons (or protons) in the universe, and R the equilibrium radius of the universe. Write

$$ds=R\,d\chi_s=(R/\sqrt{N})\,d\theta_s. \tag{2.5}$$

Then (2.4) becomes

$$\{\alpha\,(iE_s\,\partial/\partial\theta_s)+1\}\,\psi=0. \tag{2.6}$$

3. The angle $d\chi_s=ds/R$ would seem to be the natural reckoning of ds, avoiding the introduction of an arbitrary and irrelevant unit such as the standard metre. But this may seem to be taking the geometrical representation of world-curvature too literally, and, moreover, it is not immediately obvious why the *equilibrium* radius of the world should be the natural unit. We can, however, see in another way that $d\chi_s$ is the fundamental reckoning. The radius R has a general importance because it is equal to $\lambda^{-\frac{1}{2}}$, where λ is the cosmical constant. Hence

$$d\chi_s{}^2=\lambda\,ds^2=\lambda g_{\mu\nu}\,dx_\mu\,dx_\nu=R_{\mu\nu}\,dx_\mu\,dx_\nu, \tag{3.1}$$

the law of gravitation being $R_{\mu\nu} = \lambda g_{\mu\nu}$. In the affine field-theory $R_{\mu\nu}$ is the fundamental in-tensor and $R_{\mu\nu}\, dx_\mu\, dx_\nu$ is the affine invariant associated with a displacement.* Thus in using $d\chi_s$ as the measure of a displacement we not only avoid introducing an arbitrary unit of length but avoid all reference to Riemannian metric. This is an important condition, for clearly the definitions and conventions of macroscopic (Riemannian) measurement of space should arise out of the microscopic equations of electrons and protons and not be assumed in formulating them. The fact that (2.6) involves only the *affine invariant* (independent of gauge) strengthens our belief that it is approaching something really fundamental.

From an analytical standpoint the essential relation between a proton and electron should be most clearly exhibited if we treat the simplest possible "universe" consisting of one proton and one electron. In that case $N = 1$ and $d\theta_s = d\chi_s$, so that $d\theta_s$ is the affine measure of the displacement. But from a physical standpoint this may be an over-simplification, since many of the ordinary physical concepts become indefinable in so simple a universe. We can at any stage return to a more comprehensible universe with N protons and N electrons by the transformation $d\theta_s = \sqrt{N}\, d\chi_s$, so that $d\theta_s^2 = NR_{\mu\nu}\, dx_\mu\, dx_\nu$. This means that when, instead of referring to a unique electron, we can only refer to "one of N indistinguishable electrons," or, geometrically, when besides giving a point position in a co-ordinate system we attach to it one of N possible labels, the affine invariant $R_{\mu\nu}\, dx_\mu\, dx_\nu$ is replaced by $NR_{\mu\nu}\, dx_\mu\, dx_\nu$.

4. The constant α in (2.6) is the only numerical factor in the equation and it ought not to be difficult to discern its origin in the geometry of the problem. My series of investigations originated in the belief that α represents the number of relativity rotations or degrees of freedom of the system,† and this interpretation has been adhered to in all subsequent developments. A system of two charges has 136 relativity rotations of the ordinary type together with an additional rotation representing change of gauge. Thus in the problem of interaction of two charges whose positions are referred to Riemannian space, $\alpha = 137$ in close agreement with experiment. I have not yet gone into the matter thoroughly, but, so far as I can see, the rotation corresponding to gauge transformation is not concerned in (2.6); we have already seen that it is a purely affine equation which does not introduce gauging or Riemannian geometry. I take, therefore, $\alpha = 136$ as the appropriate value in (2.6). It

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* Eddington, "Mathematical Theory of Relativity," § 95.

† 'Proc. Roy. Soc.,' A, vol. 122, p. 358 (1929).

is quite possible that a factor 137/136 will be introduced later on in transforming the results for affine space into our practical reckoning in metrical space ; so that, if we had nothing further to learn from the discussion of the affine equation, we might as well transform it to practical reckoning straight away by writing $\alpha = 137$.* But our aim here is to study the fundamental relations, and it would be fatal to this purpose to introduce the " packing factor " 137/136 out of its proper order in the sequence of development.

We use the number of relativity rotations of *two* charges primarily because this is obviously appropriate to the " universe " consisting of one proton and one electron that is being considered. But the same number has a much wider application owing to the fact that the basis of affine geometry is an elementary displacement dx_μ. Such a displacement is a relation between two points, and a point only comes into consideration as being the possible seat of electric charge. Thus dx_μ as it occurs in microscopic physics is essentially a relation between two charges, and has the degrees of freedom of a system of two charges directly associated with it.

Inserting $\alpha = 136$ in (2.6), we have

$$\{136\,(iE_s\,\partial/\partial\theta_s) + 1\}\,\psi = 0. \tag{4.1}$$

5. Instead of Dirac's linear Hamiltonian we often use a quadratic Hamiltonian of Schrödinger's type. The quadratic Hamiltonian is

$$\frac{1}{\mu}\,(p_1{}^2 + p_2{}^2 + p_3{}^2 + p_4{}^2) = -\,\frac{h^2}{4\pi^2\mu}\left(\frac{\partial^2}{\partial x_1{}^2} + \frac{\partial^2}{dx_2{}^2} + \frac{\partial^2}{\partial x_3{}^2} + \frac{\partial^2}{\partial x_4{}^2}\right) \tag{5.1}$$

The constant μ is not of absolute importance until we decide the arbitrary factor contained in the wave equation. For plane waves in the direction s, the second order wave equation reduces to

$$\left(\beta\,\frac{\partial^2}{\partial\theta_s{}^2} + 1\right)\psi = 0, \tag{5.2}$$

where we use natural measure $d\theta_s$ as before and β is a positive numerical coefficient.

In the second order wave equation ψ may be a single quantity or a group of components, but in the latter case the components do not interact with one another or " rotate " and they effectively behave as a single quantity. The 136 rotations of Dirac's ψ (which has 16 components) are not involved. In fact the electrical characteristics of the particle are ignored altogether and we may say that Schrödinger's form of equation refers to " mechanical particles " without any electrical properties.*

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* For this reason 137 seems to be the right value (or very nearly the right value) to use in the theory of the cosmical constant, as implied in my paper.

An equation of the form (5.2) can be deduced immediately from (4.1). I wish, however, to discuss the equation on its own merits as not in any way connected with electrical particles, but describing an ideal neutron or mechanical particle. Following the same rule as in determining α, we must take β to be the number of relativity rotations or degrees of freedom which arise in a theory of mechanical particles. The question is perhaps more ambiguous than in § 4, but the possible alternative suggestions all seem to lead to $\beta = 10$. The 136 degrees of freedom were associated with a displacement whose extremities were considered to be the sites of electrical particles; if we substitute mechanical particles, displacement appears in its ordinary aspect as a relation which is wholly representable in Riemannian space-time. As is well-known, Riemannian geometry comprises mechanics so that the mechanical relation expressed by displacement is equivalent to the geometrical relation. A geometrical displacement (in Riemannian geometry) has 10 degrees of freedom, viz., 6 rotations and 4 translations; the latter are equivalent to rotations in the direction of a fifth dimension, regard being had to the curvature of space-time. Alternatively, since (5.2) is a second order equation, we ought perhaps to take the degrees of freedom of $ds^2 = g_{\mu\nu}\, dx_\mu\, dx_\nu$. This admits 10 independent variations $\delta g_{\mu\nu}$.

Arguments might perhaps be adduced in favour of $\beta = 6$, *i.e.*, the number of relativity rotations of an Einstein spherical world. Undoubtedly a fuller investigation will be necessary to justify fully our assumption that $\beta = 10$; but that may well be postponed.

Our ideal neutron accordingly obeys the equation

$$\left(10\frac{\partial^2}{\partial\theta_s^2} + 1\right)\psi = 0. \tag{5.3}$$

By comparison with (4.1) we see that its proper mass is $136/\sqrt{10}$ times that of the particle there described, viz., the electron. This makes the mass of the ideal neutral particle very nearly $\sqrt{(\mathrm{M}m)}$ where M and m are the masses of the proton and electron.

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* In so far as the interactions of electrical particles are replaceable by a mechanical energy, they can be dealt with by a purely mechanical equation. Thus Schrödinger's equation is extended to deal with electrical problems by inserting empirical terms to represent the mechanical energies introduced.

I do not, of course, suggest that neutrons actually exist. They appear as a half-way stage in passing from geometry to physics, geometrical points being first replaced by mechanical neutrons which are afterwards to be modified by electrical properties.

6. If we follow strictly the idea of the relation of the proton and electron indicated in my "Preliminary Note," we regard (4.1) and (5.3) as really describing the same thing, the change of mass in the ratio $136/\sqrt{10}$ being a distortion introduced in representing displacements with 136 degrees of freedom in a space-time admitting only 10. If we can describe an antitropic entity whose mass simultaneously undergoes the opposite distortion $\sqrt{10}/136$, we can account for the proton, since the mass ratio of proton and electron is nearly $136^2/10$.

Unfortunately for this line of explanation, the masses m and $\sqrt{Mm}$ are found to occur the wrong way about. The fundamental microscopic equation (4.1) should have given the mass $\sqrt{Mm}$, which could then be distorted oppositely into M and m by our representation in space-time with fewer degrees of freedom. Actually (4.1) gives the mass m, as shown in my investigation of the cosmical constant. We must therefore seek a different kind of relation between the Hamiltonians of (4.1) and (5.3) if any part of the idea is to be retained.

If one Hamiltonian is not a replacement of the other the natural suggestion is that both represent energy that must be included in the equation. By (2.3) $(iE_s^2) = 1$; hence the proposed combination of (4.1) and (5.3) can be written

$$\left\{10\left(iE_s \frac{\partial}{\partial\theta_s}\right)^2 + 136\left(iE_s \frac{\partial}{\partial\theta_s}\right) + 1\right\}\psi = 0. \tag{6.1}$$

The suggestion proves to be immediately successful, and perhaps no other defence is needed. We shall, however, consider what is implied in adding the two Hamiltonians. It clearly means that the relation of the electrical system to space-time gives it 10 external degrees of freedom with additional energy corresponding thereto. (We had previously been supposing that these were merely a distorted representation of the 136 internal degrees of freedom—an idea which had some plausibility because certain internal rotations of the system are equivalent to rotations of the co-ordinate frame.) This recalls our earlier remark that the universe consisting of one proton and one electron is an over-simplification. It contains just enough differentiation to provide two ends to a displacement, but nothing external to relate the displacement to.

When more charges are present a displacement, besides involving the electrical relations of the two particles at its ends, also involves the relations of these to the averaged states of the other particles in the universe, and it is because of these external relations that there is a meaning in representing it as having a position and direction in macroscopic space-time. The space-time field (or inertial field) is the smoothed equivalent that we have substituted for the averaged effect of the unspecified particles in the universe.*

7. When resolved into factors (6.1) becomes

$$(135\cdot9264\, i\mathrm{E}_s\, \partial/\partial\theta_s + 1)\,(0\cdot0735692\, i\mathrm{E}_s\, \partial/\partial\theta_s + 1)\, \psi = 0, \qquad (7.1)$$

which yields two alternatives

$$(135\cdot9264\, i\mathrm{E}_s\, \partial/\partial\theta_s + 1)\, \psi = 0, \qquad (7.21)$$

$$(0\cdot0735692\, i\mathrm{E}_s\, \partial/\partial\theta_s + 1)\psi = 0. \qquad (7.22)$$

The first is almost the same as (4.1), so that we may take it to be the wave equation for an electron, (4.1) being a less accurate approximation. The second equation corresponds to a particle of mass greater than that of the electron in the ratio 135·9264 : 0·0735692, or 1847·60. This agrees closely with the proton.

Accordingly (6.1) appears to be the wave equation which is satisfied by electrons and protons. It should be noted that it is the equation for an electron *or* proton, not an electron *and* proton.

8. It remains for us to show that the charges of the two kinds of particles satisfying (6.1) have opposite sign. To test this we have to introduce an electromagnetic field, which will be represented by an additional term in the equation. We shall assume (as a definition of a macroscopic electromagnetic field) that this additional term is of the same form as in Dirac's and Schrödinger's equations, viz., it does not involve $\partial/\partial s$ or $\partial^2/\partial s^2$ though (in Dirac's theory) it may contain matrices. The field is accordingly introduced by altering the third term from 1 to $1 + \mathrm{F}$.

Since the first two coefficients of the quadratic are unaltered the sum of the roots is unaltered. Accordingly, the sum of the masses or energies of the two possible particles is not altered by an electric field. If the field adds an energy $e\phi$ to the proton it adds an equal and opposite energy $-e\phi$ to the electron. More generally, when F involves matrices, the addition to the roots will involve matrices and be interpreted as additional momentum as well as energy ; but the addition is always equal and opposite for the electron and proton. This is just what is meant when we say that their charges are equal and opposite.

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* 'Proc. Roy. Soc.,' A, vol. 133, p. 606 (1931).

9. The value 1847·6 of the mass-ratio which is here obtained is closer to the observational determinations than the value 1849·6 given in my "Preliminary Note." A recent discussion by W. N. Bond* gives 1846·6 ± 0·5 as the observational value; but many physicists incline to a value several units smaller. I do not think the question of exact agreement is very important at this stage of the theory.

Taking together this theory of the proton and the theory of the cosmical constant, the only numerical coefficients employed are the freedom-numbers 136 and 10. The equations throughout are of the simplest type and all linear measure is expressed in terms of the fundamental affine invariant. The equations yield a ratio of the masses of the electron and proton which is at any rate within 0·3 per cent. of the observational value. They give also the absolute masses (in natural units) in agreement with observation; in this case there is only a rough test of agreement since the observational value has a probable error of the order 10 per cent., but the extreme magnitude of the quantity to be checked (about 10^{39}) makes even the rough agreement a rather severe test.

Although we do not enter here into the theory of the occurrence of freedom-numbers in the equations, it is to be noted that their use is not an *ad hoc* principle invented for the present discussion. The freedom-number was introduced and provisionally accounted for in my earlier papers; it was first suggested by two quite independent constants, viz. the fine-structure constant and the packing-fraction. The discovery of additional instances of the appearance of freedom-numbers should facilitate the investigation of the precise theory underlying them.

Summary.

From the theory of the cosmical constant developed in a previous paper it appears that the wave equation for an electron with momentum vector in the direction s is

$$(136\, i\mathrm{E}_s\, \partial/\partial\theta_s + 1)\, \psi = 0. \tag{1}$$

Here $d\theta_s$ is the natural measure of a displacement as given by the affine field-theory, $d\theta_s^2$ being the affine invariant $\mathrm{NR}_{\mu\nu}\, dx_\mu\, dx_\nu$; the factor N represents the number of electrons (or protons) in the system.

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* 'Phil. Mag.,' vol. 12, p. 632 (1931).

Reasons are given for supposing that this equation is incomplete, and that the correct equation is

$$(10\,(i\mathrm{E}_s\,\partial/\partial\theta_s)^2 + 136\,(i\mathrm{E}_s\,\partial/\partial\theta_s) + 1)\,\psi = 0, \qquad (2)$$

the factors 10 and 136 representing the number of degrees of freedom associated with the respective energy terms. The mass m of a particle satisfying this wave equation is given in natural measure by

$$10m^2 - 136m + 1 = 0,$$

or, in factors,

$$(135 \cdot 9264m - 1)\,(0 \cdot 0735692m - 1) = 0.$$

The two roots evidently correspond to electrons and protons, and their ratio is 1847·60. It is verified that the two roots represent charges of opposite sign. Since the mass of the electron given by (2) and (1) is almost the same, the calculation of the cosmical constant is unaffected.

Address of the President, Sir Frederick Gowland Hopkins, at the Anniversary Meeting, November 30, 1931.

It is right that at our Anniversary Meeting we should have in mind the losses that our Fellowship has suffered during the year that has just passed. We have to deplore to-day the deaths of no less than four of our distinguished Foreign Members, together with fourteen Fellows of the Society.

ALBERT AUGUSTE TOUSSAINT BRACHET, of Brussels, was a distinguished leader in the science of embryology. He was one of the pupils of van Beneden and carried on traditions derived from that master of the subject, though on lines of his own. His earlier work dealt chiefly with the morphological facts of development, but he later made important contributions to experimental embryology. His researches were specially concerned with the early stages of development in the amphibia, and his work threw important light upon the problem of localisation in the developing egg. His later interests and contributions were concerned with what may be described as the physiological factors and conditions which initiate development. He was elected as a Foreign Member of the Royal Society in 1928.

MARTINUS WILLEM BEIJERINCK. The experimental researches of this distinguished Dutch biologist covered an extraordinarily wide field; they broke much ground that was new, and almost always led to results of high importance. He is best known, perhaps, for his discovery that the root nodules of papilionaceous plants are caused by an organism which he succeeded in cultivating outside the nodules and called *Bacillus radicicola.* This discovery, and Beijerinck's own further work on the subject, were of fundamental importance in demonstrating and explaining the biological fixation of nitrogen. His researches on other aspects of bacteriological metabolism were also of the greatest interest: his studies, for instance, of luminous bacteria, of the oligonitrophilous and oligocarbophilous organisms; of an organism which, while liberating nitrogen from nitrates, obtains its energy by oxidising sulphur. This is but one example of many investigations all tending to illustrate remarkable diversities in the metabolism of living cells. His work on the mosaic disease of the tobacco plant first introduced a knowledge of viruses into

Western Europe. Beijerinck was a learned botanist, and almost as well qualified as a chemist. Much of his work indeed was done in fields other than those described. It was always illuminating. He became a Foreign Member of this Society in 1926.

ALBERT ABRAHAM MICHELSON. This highly-gifted physicist is doubtless best known for his share in the classical Michelson-Morley experiments contrived to detect any possible effects of the earth's rotation upon the velocity of light. In his younger days Michelson was instructor in physics and chemistry under Admiral Sampson at the American Naval Academy. Later he studied in Berlin and Heidelberg, and also in Paris. On his return to the United States in 1883 he held chairs at Cleveland, Ohio, and at the Clark University, and finally in 1892 went to the Chair of Physics at Chicago. In 1925 he was appointed to the first of the Distinguished Service Professorships instituted by the last-mentioned University. It was in Optics that Michelson always excelled, and he seems to have been from the first attracted to the study of the interference of light, a preference on his part which proved fortunate for physical science. In the use of the interferometer he was a magician. In 1890 he first suggested that interference methods might be applied to astronomical problems. His grasp of this technique and his sense of its possibilities led to great results, one of which may receive special mention. Eddington had made the prediction, for adequate reasons, that a star like Betelgeuse must have the dimensions of a solar system, and by using data available from his own theory of stellar constitution he made an estimate of the probable diameter of that star. To the direct measure of the angular dimensions of Betelgeuse Michelson's interferometer was now applied. The capacity of the instrument proved equal to expectations and the observers realised that for the first time they had been able to measure the angular dimensions of a star. An estimate of its distance gave the actual diameter and Eddington's estimate was confirmed. Interferometric methods have doubtless yet many and important applications before them. For the study of atomic radiations Michelson designed a very successful instrument, the Echelon Spectroscope. The famous Michelson-Morley experiment called, of course, for the utmost refinement of measurement, and in that art Michelson was supreme. The result formed, as we know, the very basis of Relativity. Michelson became one of the Foreign Members of this Society in 1902, and was awarded our Copley Medal in 1907.

Baron KITASATO. Kitasato was one of the greatest among bacteriologists. So far back as 1889, his success in obtaining for the first time pure cultures of the tetanus bacillus reduced the etiology of that disease to a clear issue, and when in the next year he, conjointly with Behring, discovered an antitoxin for tetanus in the blood of animals, he helped to lay the foundations of serum therapy, and prepared a way for saving innumerable lives. In 1894 he discovered the bacillus of plague and described with complete accuracy all its essential properties. He advanced his science along many other notable lines. Kitasato first studied Medicine at Tokyo, and in 1885 was sent by the Japanese Government to study under Robert Koch at Berlin, where he was recognised as perhaps the most brilliant disciple of that master. After carrying out in Germany a great number of high-class researches, he returned to Japan in 1891. A few years later the Imperial Japanese Institute for the study of Infectious Diseases was founded by the Government, and was under the charge of Kitasato for fifteen years. It attained to great success and prestige. For his services to science and his country Kitasato was, in 1923, ennobled and given the title of Baron. He was admitted as a Foreign Member of the Royal Society in 1908.

ALFRED BARNARD BASSET, a mathematician, was free from the necessity of adopting a profession and devoted himself to research. From 1897 onwards he produced a succession of papers dealing with such subjects as the equilibrium of revolving fluids, the theory of elastic plates and shells, the variable slow motion of a sphere in a viscous fluid, and with many other aspects of applied mathematics. His work was distinguished throughout by an exceptional command of analytical methods. He was the author of several able treatises which at an earlier period were devoted to applied and later to pure mathematics. He was elected a Fellow of the Royal Society in 1889, and was Vice-President of the Mathematical Society in 1892–93.

Sir OTTO BEIT, though not himself engaged in scientific pursuits, was one to whose enlightened generosity medicine and its allied sciences owe a great debt. In 1909 he established a Foundation as a memorial to his brother, Mr. Alfred Beit, and endowed it with a personal gift of nearly a quarter of a million sterling. This Foundation supports a number of carefully selected research workers, known as Beit Memorial Fellows, whose work during the last thirty years has made valuable contributions to many branches of knowledge bearing directly or indirectly upon the advance of practical Medicine. Few laymen have had such a clear understanding of the necessity and nature of research as Sir Otto Beit possessed, and he took care that the activities of those who benefited by his generosity should be free from inhibitions due to inelastic regulations and requirements. He made other large gifts for the furtherance of clinical medicine itself; in particular, for the provision of adequate supplies of radium at the London Hospitals. His services to science were recognised by the Royal Society in his election to the Fellowship in 1924.

Lord MELCHETT (ALFRED MORITZ MOND) for some years, and especially after the War, was a dominant personality in enterprises which in this country have sought to apply science, and especially chemical science, to industry. He was a youth when his father, Dr. Ludwig Mond, was developing the activities of the great chemical firm of Brunner Mond, so that inheritance and early impressions prepared him for success in the later stages of his career. For a time he practised at the Bar, and in 1906 entered politics, which long occupied most of his time. In 1925, however, he returned to chemical industry, in the development of which he played so great a part. He often expressed his faith that it is the chemist who will solve the present economic and industrial problems of the world. His latest enthusiasm was for the rationalisation of industry, and the great combine, " Imperial Chemical Industries ", was largely an outcome of that enthusiasm.

Sir CHARLES ALGERNON PARSONS. It is due to the genius and firm faith of Charles Parsons that the steam turbine now produces practically all the electricity derived from steam power, and that every fast ship of large size, both naval and mercantile, is driven by steam turbines. This great end was attained slowly and in the face of many difficulties, but the creator of the turbine was never stopped by difficulties, even if at first they might seem insuperable. Apart from his engineering work, Parsons had wide scientific interests. Inherited from his father, Lord Rosse, was a special concern with optical work. He himself devised greatly improved methods for producing search-light reflectors, and the Heaton works, an enterprise started by himself at Newcastle-on-Tyne, came to make nearly all the parabolic reflectors produced in Great Britain. His attempts to make diamonds artificially, though unsuccessful, illustrated his courageous spirit and experimental enterprise. He believed very firmly in the importance of research in industry, and never grudged expenditure upon it. He was the Rumford Medallist in 1902, and in 1928 received the Copley Medal. He was a great man who served his generation nobly.

WILLIAM CARMICHAEL MCINTOSH, a marine zoologist, who died at the great age of 92, was for many years engaged in studying the invertebrate fauna of the North Sea. In 1873–74 the Royal Society published the first volume of his great monograph on British marine annelids. This volume dealt with the nemertines, and its great merits received full recognition both in this country and abroad. The remaining volumes of the monograph, dealing with the polychaetes, were unfortunately not published till many years later, and made less impression. In 1882 McIntosh was appointed to the chair of Natural History at St. Andrews and was shortly afterwards selected by a Royal Commission for the duty of enquiring into the problems raised by the introduction of beam trawling and its effect upon the sea fisheries. His keen pursuit of this work led to his establishing at St. Andrews the first marine laboratory in Great Britain. It was a modest establishment, but during its existence it gave opportunities for study to many zoologists of distinction. McIntosh and his pupils played a large part in the researches which showed that all marine food fishes except the herring have pelagic floating eggs. The proof of this, and their careful description of eggs and larval stages, were of importance in their practical bearings. McIntosh received a Royal Medal in 1899.

JAMES LORRAIN SMITH, a pathologist, who is best known to students of science from his early work with J. S. Haldane on hæmoglobin and its relation to carbon monoxide, which led to a practicable method of determining in man the volume of the blood and the total quantity of circulating hæmoglobin. This method was applied by Lorrain Smith himself to the investigation of human anæmias and yielded interesting results by showing that in pernicious anæmia there is a substantial reduction of hæmoglobin, whereas in chlorosis there is no such shortage but only a dilution of the blood with excess of plasma. In conjunction with Mair he devised two histological methods of value—the Nile blue sulphate stain for neutral fats and fatty acids, and an improvement in Weigert's method which made it suitable for the demonstration of tissue lipoids. Smith attained to distinction in philosophy in his undergraduate days and he remained perhaps more a philosopher than an experimentalist. Nevertheless, on the more technical aspects of his subject he did much sound work. He held successively the chairs of pathology at Belfast, Manchester and Edinburgh.

WILLIAM DOBINSON HALLIBURTON. Halliburton was, in this country, a pioneer in the field of physiological chemistry. If he cannot be said to have made fundamental discoveries in that branch of science, he did sound work for it at a time when it was largely neglected alike by English physiologists and chemists. In later years he turned rather to physiological experimentation. His work upon the cerebrospinal fluid, published in conjunction with W. E. Dixon, reached a high order of merit. Halliburton was an admirable teacher and his stimulating influence upon many pupils during his long tenure of the chair of Physiology at King's College, London, was of much service alike to physiology and biochemistry. His " Text Book of Chemical Physiology and Pathology," published so far back as 1901, was then the only work of its kind in English, while other books written by him since, and especially the nineteen successive editions of his "Handbook of Physiology," have long served in the education of medical students. He became a Fellow of the Royal Society in 1891. An unfortunate failure in health removed him from active life for nearly nine years before his death.

CHARLES THOMAS HEYCOCK. Heycock's work upon metals and their alloys, done throughout in conjunction with his lifelong friend, F. H. Neville, and lasting for more than a quarter of a century, was of the utmost scientific importance. The first of the conjoint papers was published in 1889, and dealt with the depression of the freezing points of metals induced by others dissolved therein. Further observations were published in later papers and the authors showed that the addition of small amounts of a second metal depresses the freezing point of the first to an extent which is directly proportionate to the atomic or molecular weight of the added metal. Raoult's law for ordinary solutions was proved to hold for alloys. A method was also indicated for calculating the latent heat of fusion of a metal by an application of the van't Hoff equation to the freezing point depression. The invention by Callendar of the platinum resistance pyrometer rendered valuable assistance to the researches; the melting points of many metals in the pure state were determined, and later those of mixtures of metals in all proportions. The results interpreted by the phase rules of Willard Gibbs and Rooseboom were supplemented by the microscopic examination and photography of the polished and etched surfaces of the solidified alloys. Heycock, like his colleague, was a fine technician, and the work done was of the highest degree of accuracy. It attracted the interest of the Goldsmiths' Company, who endowed a Readership in Metallurgy at Cambridge, an office which Heycock held for twenty years. He was elected to our Fellowship in 1895 and was awarded the Davy Medal in 1920.

HERBERT TOMLINSON, while Lecturer in Natural Philosophy at King's College, London, carried out a series of researches on the influence of stress and strain on the physical properties of matter, on moduli of elasticity for example, and on electric conductivity; and also the effect of magnetisation on the elasticity and internal friction of metals. Between the years 1885 and 1894 he published upwards of forty papers upon such subjects. He was elected a Fellow in 1889.

ARCHIBALD BARR. Professor Barr was an eminent engineer of great inventive ability to whom the country was greatly indebted during the War for the prominent part he took in supplying technical equipment to the fighting services. Many of his own inventions at this time added much to the efficiency of that equipment. One of his first important inventions, worked out in 1888 in conjunction with his then colleague, William Stroud, was the modern range-finder. In 1905 Barr invented a step-by-step motor for signalling electrically from range-finder to gun. In later years other instruments were designed and the intricate fire-control system of the modern warship is based upon Barr's enterprises. In 1889 he returned to his own University of Glasgow as Regius Professor of civil engineering and mechanics. As the results of his efforts the James Watt Engineering Laboratories were opened in the following year. So inspiring was his teaching there that his school at Glasgow rapidly attained to fame.

Walter Ernest Dixon had an international reputation as a pharmacologist, and was a member of the League of Nations Committee on drugs of addiction. His scientific work covers a wide ground involving many studies of drug actions. Outstanding was his work with Brodie upon the bronchial muscles and vasomotor nerves of the lung, directed to explain the nature of asthma; and also his studies of the secretion and circulation of the cerebrospinal fluid. Dixon at one time held the chair of Pharmacology at King's College. He was made Lecturer in his subject at Cambridge in 1909, and ten years later was given the office of Reader.

Sir Thomas Stanton as an engineer was noted for his continuous activity in research and for his skill in applying laboratory methods to engineering problems. His personal investigations were made in many fields, including, for instance, the effect of wind pressures upon structures, the resistance of materials to intermittent stresses, lubrication, the heat transfer and friction between solid surfaces and moving fluids, and the movement of projectiles at speeds exceeding the velocity of sound. After holding academic positions at Liverpool and Bristol, he joined in 1901 the Staff of the National Physical Laboratory, where he built up the Engineering Department from small beginnings to its present eminence. For some years he had also charge of the aero-dynamical work of the laboratory.

Percy Groom, a botanist who did valuable work on the morphology of flowering plants, but who will perhaps be best remembered by his application of botanical knowledge to economic problems. He published many papers on timbers and forestry topics, and on the diseases which affect wood in various circumstances. An investigation which was still in progress when he died dealt with mildew as affecting book covers. This was undertaken on behalf of the Public Record Office. He held the chair of the technology of woods and fibres at the Imperial College of Science and Technology.

Sir HOWARD GRUBB devoted a long and active life to the design and manufacture of astronomical and other optical instruments. To such enterprises he applied profound scientific knowledge and instinctive ingenuity. His father, Sir Thomas Grubb, who also possessed great skill in the art of lens and mirror making, was elected to the Fellowship of the Royal Society in 1864. Howard Grubb built the 27-inch refractor and three domes for the Vienna Observatory between 1878 and 1881, and during subsequent years produced refractors of large diameters for Cape Town, Oxford, Greenwich, and other observatories. During the early nineties he constructed seven 19-inch photographic refractors for the International Survey of the Heavens, a task which presented exceptional technical difficulties. In connexion with all such enterprises, many and various advances in technique were due to him. In 1905 he invented the submarine periscope which was adopted by the Royal Navy, and he made 94 per cent. of these instruments as used in the War. In later years he was closely associated in both scientific and commercial enterprises with Sir Charles Parsons, upon whose death his own followed so closely.

Sir DAVID BRUCE. Major-General Sir David Bruce was one of a relatively small band of investigators who, towards the end of the last century, laid solid foundations for tropical medicine. His early work upon the etiology of Malta fever displayed his high qualities as an investigator and led to the practical control of a very troublesome disease. Later he investigated the diseases known as "nagana" and "tsetse-fly disease." These were supposed to be distinct, but Bruce demonstrated their identity, both, as he showed, being caused by a trypanosome. He then proved that the parasite was carried and transmitted by the tsetse-fly. In 1903 he went at the request of the Royal Society to study sleeping sickness in Uganda, and did successful and important work in making clear its etiology.

Before turning to other matters, I cannot refrain from making regretful reference to the illness of our Assistant Secretary, Mr. F. A. Towle. All our Fellows who have had contact with him, or have sought his help in any way, will have recognised the qualities that have made him an admirable permanent official of the Society. He has taken great personal pride in its activities, always being careful, where it lay in his power, to protect its interests and its prestige. To the Officers his organising ability and his grasp of detail have been invaluable. One of his recent tasks, very thoroughly carried out, was the preparation of the new catalogue of the portraits in the possession of the Society. All will most sincerely hope that Mr. Towle's health may be re-established. Mr. R. Winckworth now holds the position of Acting Assistant Secretary.

In reviewing briefly the activities of the Society during the year, I will first refer to the disposal of our Trust Funds. Lord Rutherford, in his Address last year, discussed the reasons for the Council's recent policy in respect of these. A period of conservative treatment of the Funds, justified at the time, had led to an accumulation of capital, and, as stated in its Report of last year, the Council, upon consideration, decided that the time had arrived when the holdings entrusted to the Society should be freely expended, in accordance with the donors' intentions, upon the active support of current researches of fundamental importance. Lord Rutherford described the progress of that policy up to the date of his last Address. This year's Council, as I shall immediately point out, has continued to apply it. That it is justified few, if any, will deny; its results will, I think, prove its wisdom. It should be fully understood, however, that the Society has no longer considerable balances of unallotted income in its hands; not even in its major trusts, such as the Messel and Mond Funds. I am sure, however, that the desire of the Society to do all that is financially possible for the support of individual research nevertheless remains.

The Council has this year made the following grants: From the *Messel Fund:* £800 a year for five years to Dr. Honor B. Fell, of the Strangeways Research Laboratory, for the support of her valuable work on Tissue Culture; also £150 for the current year, and, after the termination of his 1851 Exhibition Scholarship, £600 a year for two years to Dr. M. L. Oliphant, of the Cavendish Laboratory. From the *Caird Fund:* £2,200 to Professor O. W. Richardson for the purchase of optical apparatus of high resolving power. From the *Donation Fund:* £400 to Dr. L. S. B. Leakey towards the cost of his East African Archæological Expedition. From the *Darwin Fund:* £500 a year for four years to Mr. C. S. Elton for research on wild vole populations, together with an additional grant of £250 for capital outlay and field equipment.

I may remark here that Dr. Adler's researches on Kala-azar in Mediterranean countries, mentioned in Council's Report last year, continue to receive support from the Anonymous Bequest Fund.

During the year the Society has received three bequests—one of £10,000 from Sir Otto Beit, a second of £3,000 from the estate of Dr. A. Muirhead, and a third of £275 from that of Dr. C. W. Andrews. These bequests were left without restrictions, and have been added to the General Fund.

It is satisfactory to be able to report that, arrangements with the University of Cambridge being complete, the Cryogenic and Magnetic Research Laboratory referred to in last year's Address will now come into being as the "Royal Society Mond Laboratory." This title secures recognition of the circumstance that the Society was able to forward the enterprise through its possession of Dr. Ludwig Mond's benefaction. Further details of the arrangements will be found in Council's report.

The conditions under which grants have been made to individuals for the purchase of valuable apparatus have hitherto been inadequately defined. Council has been wise, I think, in deciding that the use of such apparatus shall be under the control of a "Scientific Apparatus Committee," in which will be merged the committee which now controls the Society's store of radium. The applicant for whom such valuable apparatus is originally purchased will not be regarded as having a vested interest in it beyond the first full year after delivery.

I do not need to remind you that at the Special General Meeting of Fellows, held at the close of last year, it was decided not to request the Council to alter their decision to modify Statute 5. This statute now so reads as to allow the Council to nominate seventeen candidates annually for election to the Fellowship, and, as you are aware, seventeen new Fellows were duly elected in May last. I believe that those of you who have cared to give further thought to the matter during the months which have since passed, will, whatever your first reaction, have become convinced of the wisdom of this essentially conservative change in our Statutes. There can be no question from what was said at the General Meeting that the Fellows in general desire that the Council should henceforth exercise its statutory power of nomination with greater freedom and over a wider range than has been their custom of late years. More difficult to estimate was opinion concerning the direction of such increase in range. If there be differences of opinion on this point, I would like to state my profound conviction that so great is the sense of responsibility felt and displayed by every member of each successive Council when nominations are the issue, that the interests of the Society itself, like those of every individual candidate; will continue to be safeguarded. In my opinion no real conflict between collective interests and individual claims can ever arise.

I may now be allowed to follow custom and say a few words concerning current scientific progress. My distinguished predecessor, as was natural and proper, dealt in successive Addresses with aspects of physical science. It is for me to turn your attention to biological matters.

Prominent to-day is a call for trained biologists in the economic sphere. They are urgently required for the service of the Empire. A little while ago it was somewhat suddenly realised by administrators that for the successful development of some of our most promising Colonies, and indeed for the solution of not a few economic problems at home, the practical application of a sound biological knowledge had become essential. In many wide districts of the Empire ubiquitous parasites in their legions hold sway over human destiny, and in some districts these diverse legions form the only factor limiting economic progress. The application and the development of biological knowledge can alone solve the problems that thus arise. Tropical climates indeed present many other environmental problems distinct from the example mentioned which call for the aid of biological science. There are to-day indeed still great opportunities for the systematist, the ecologist, the economic entomologist, and for field naturalists in general to apply their knowledge in this service.

It is however of the progress of experimental biology, more closely defined, that I wish in particular to speak. Although at least one generation of investigators has been busy in applying the method of controlled experiment to the analysis of living organisms, yet relatively at least the method is new to biology, and there are still those who for one reason or another mistrust its application. You are doubtless familiar with the philosophic attitude of which we have heard a good deal of late, and which in some quarters has achieved the name of Holism. Most of its implications are doubtless metaphysical, but it is apt to involve explicitly or implicitly a distrust of all attempts to study a living organism otherwise than in its integrity. Apart from those who are obsessed by this holistic philosophy, there are still professed biologists whose minds, being adjusted to morphological and descriptive studies, or to the study of behaviour in the organism as a whole, are out of sympathy with the analytical methods of experiment.

I think, however, it is not going too far to claim that recent progress in experimental biology, though to a superficial view less impressive, has been not less significant, and indeed not less revolutionary than the progress of modern physics. I might support this claim in many ways. It is, I think, justified in that region of knowledge where cytology and genetical studies meet together. It is now, of course, some years since the reaping of significant facts from this field began, but the harvesting actively continues and the store is growing rapidly. That inherited characters as displayed by plant or animal are transmitted as particulate factors, segregated in one generation and regrouped in the next—inheritance being, so to speak, atomic—has become common knowledge since the first rediscovery of the work of Mendel. That each factor or gene so inherited has an objective determinant which can be seen and identified as a material unit of structure in germ or sperm is also, I think, well known. That the progressive behaviour and the interactions of such units of structure can be followed during development; that the presence or absence of certain among them determines sex; that the reason why certain characters are always inherited together as a group, while others may be segregated, is because their material determinants in the egg cell are in the former case visibly associated, while separate in the latter—such facts as these are perhaps familiar to the majority. My purpose in this reference is to emphasise the rapid growth which is to-day proceeding in this domain, and the significance of the facts which are being won on strictly experimental lines. The progress and the significance have become the greater since it was recognised that the material units I have mentioned—the chromosomes and sub-divisions of chromosomes—are "determinants" rather than "carriers" of genetic factors. It is from complex interactions of these factors with the sum total of their environment the final issues arise; but this concession to Holism detracts nothing from the significance of the experimental results. Their significance is perhaps best illustrated in this, that from the chromosome map as seen in the germ cell the display of inherited characters in the final organism may be predicted.

Unfortunately, time will not allow me to illustrate by details the progress I have claimed. I myself, indeed, have enjoyed no personal contact with the converging lines of research which have led to the present fascinating outlook in this region of science. I know enough of them, however, to wish that the facts which they have won and the methods they have used might be widely known among those whose own researches are not concerned with biological problems. They illustrate so well for other experimentalists what is peculiar in the aims, needs and methods and, I would add, the triumphs of experimental biology. One recalls the brilliant Croonian Lecture delivered by Professor T. H. Morgan in 1922 entitled "The Mechanism of Heredity." Here fundamental facts will be found and predictions of that future progress upon the occurrence of which I have insisted.

This domain of disinterested science is making many practical contacts. To mention but a single recent instance: Professor R. C. Punnett, one of the original discoverers of the phenomenon of sex-linkage in inheritance, by applying his expert knowledge of that phenomenon, has produced what may be called a synthetic fowl, of which the qualities are such as to make it of extreme value to the now highly important industry of poultry breeding and egg production. The bearing of the same body of knowledge upon human affairs has been recently very ably discussed by Professor L. T. Hogben.

The phenomena of heredity were long the stronghold of those who cling to the obscurantism of vitalistic doctrines. Infinitely complex as of course they are, we have now abundant proof that they are susceptible to analysis, and that to-day they are yielding their secrets to well-controlled experimental studies. The results of these are becoming quantitative and are even yielding material for mathematical treatment, as the interesting writings of Dr. R. A. Fisher and Professor J. B. S. Haldane have shown.

Another region in which accurate experimentation has removed, and is continuing to remove, inhibitions due to obscurantist assumptions is the physiology of the nervous system of vertebrates. It is, perhaps, too late in the day to refer to the work of Pavlov upon conditioned reflexes, though it is justifiable to emphasise its still growing influence upon thought. The work is a supreme proof of the success of the experimental method in analysing even such apparently transcendental phenomena as those which underlie the higher functions of the brain. This it has done without need of reference to psychical reactions, concerning which, as Sir Charles Sherrington remarked in one of his Addresses from the Chair, it affirms nothing and denies nothing. The nature of the transmission of events in the nervous system is receiving much illumination from the work of each of our Foulerton Professors. Professor Adrian, having developed a most admirable experimental technique for the purpose, is studying the nerve impulse and its origin with highly profitable results. He and his colleagues are now able, with great gain, to work with single nerve fibres and single isolated end organs. The apparatus for recording the transmitted potential changes in these has attained to great perfection. It involves valve amplification, and, when desirable, the conversion of the electric discharges into sound waves by a second power amplifier and a loud speaker. High frequency potential changes are recorded by means of the strikingly efficient oscillagraph designed by Professor Adrian's colleague, Mr. Bryan Matthews.

A striking circumstance, brought to light by Adrian's work and that of his colleagues, is that the nervous structures so far examined exhibit such physical regularity in their behaviour that results can often be predicted within about

1 per cent. His experiments on animals have shown how the phenomenon of grading in the contraction of muscles is controlled by the frequency of impulses sent out from the central nervous system, and by the number of nerve and muscle fibres involved. Moreover, he has been able to observe the activity of a single nerve cell in his own spinal cord by needle electrodes placed in his muscles, and finds that human voluntary contractions are regulated in exactly the same way.

Further, Adrian has found that slow potential changes occur in nerve cells and that these are connected with their discharge of impulses; so far this work only extends to isolated nerve ganglia from insects and to nerve cells in the brain stems of fish, but the phenomena he has found are extremely significant, and it seems possible that changes of potential may be of fundamental importance in the activity of nerve cells.

Adrian has found that damaged nerve fibres set up impulses at very high frequencies and these perhaps play an important part in sensations of pain, though his more recent work has made it clear that impulses in the smaller slowly conducting nerve fibres must also be concerned in the physical mechanism responsible for pain. A most striking feature of all this work is the general similarity of behaviour of nervous structures, from whatever animal they may be taken. A ganglion cell in a caterpillar (I quote Dr. Matthews) seems to work on the same general principles as a nerve cell in Adrian's spinal cord. Nature seems to have hit on sound principles for nervous structures very early in evolution, and to have gone forward to more and more complex arrangements helped by the adequacy and efficiency of these principles.

Our Senior Foulerton Professor is studying the nerve impulse from the standpoint of the thermal phenomena which accompany it. So small, of course, is the heat production in the nerve that its measurement, like that of the potential changes, calls for great refinements. Professor A. V. Hill has conquered the difficulties involved and is revealing to us the magnitude and time relations of the heat discharges involved. It is becoming clear, though we do not yet know the details of its nature, that the nerve impulse consists of a transmitted physico-chemical event, probably involving changes of ionic concentrations at membranes with consequential changes of electric potential; the whole cycle of events, comprising activity and recovery in the nerve, being supported by the energy derived from metabolic oxidative processes which, very small in scale, are associated with the cycle.

When we hope for an increase in our knowledge of the nervous system, we are always accustomed to look to researches from the laboratory of Sir Charles

Sherrington. Perusal of our B Proceedings during the last year will show that such help is still forthcoming in abundant measure. To the results published in the most recent papers from Oxford, those for instance by Professor Sherrington and J. C. Eccles, I may make the briefest reference. An extended study of reflexes has shown that the centripetal impulses do not pass straight through the spinal cord, but at central stations in the cord they are transformed into an enduring excitatory state which may in turn set up fresh nerve impulses yielding the reflex discharges. The nature of this central excitatory state is being studied by ingenious experimentation. The important results will link up, I think, with some of Adrian's observations.

I cannot refrain from mentioning here a recent research which forms a link between my discussion of the nerve impulse and the chemical considerations that I want next to put before you. It has long been suspected, though not proved, that when a sympathetic nerve is stimulated adrenaline is liberated at the nerve ending, and that the observed effects are immediately due to the action of that substance. Now our Secretary, Dr. Dale, in conjunction with a member of his staff, Dr. Gaddum, has investigated the case of the parasympathetic nerves, the influence of which in general opposes that of the sympathetic group, and had obtained good evidence that when one of these is stimulated the substance acetyl-choline, previously existing in some inactive form, is liberated at the nerve ending. The action of acetyl-choline, when injected into the circulation, resembles in general the effect of stimulating parasympathetic nerves, and there is every reason to believe that the physiological activity of the substance, rather than the transmitted physical impulse itself, is immediately responsible for the observed effects of stimulation. I may say that Otto Loewi, of Graz, has shown that when the heart beat is inhibited by vagus stimulation, a substance resembling acetyl-choline in all its known properties is actually formed in the organ, and acetyl-choline, when artificially injected, is known to produce effects like that of the vagus.

In rather unexpected circumstances we have thus brought before us an example of specific physiological effects due to the influence of the specific structure of an organic molecule. Such effects and such relations are being demonstrated in increasing diversity as fundamental factors of organisation in the animal body. This is illustrated most strikingly, of course, in the domain of the control of its activities by a group of hormones. We find in the cases of adrenaline and thyroxin, the constitution of each of which is accurately known, widely different influences depending on differences of molecular structure. The number of known hormones is now increasing and with regard to those which control the sexual and reproductive cycles, illuminating knowledge is increasing fast. I will only mention the hormonic system which correlates the activities of the pituitary, the ovum, and the uterus. In referring to this remarkable case of organisation by means of circulating chemical agencies, it is a pleasure to note how important have been the contributions to the subject which have come from Dr. A. S. Parkes, who is at present working as our Foulerton Research Student.

I may logically pass from a consideration of hormones to devote a few words to vitamins. Although, unlike the hormones, these are of exogenous origin, their activities in the body are equally potent and their functions in general as indispensable. The number of known vitamins has grown to seven or eight and the study of their functions has become a complex matter. At the same time, nobody who is in contact with the evidence doubts the reality and indispensability of these several functions. It is highly satisfactory to know that we are now within measurable distance of knowing the chemical structure of two of these substances.

We now possess proof that vitamin A is closely related to the carotenes and this knowledge may well lead, without long delay, to the artificial synthesis of the vitamin itself. With respect to vitamin D it seems probable, if not yet quite certain, that its artificial production is already accomplished. Some four years ago the constituent of animal and vegetable substances, which is converted into the antirachitic vitamin D by ultra-violet radiation, was identified as ergosterol by Rosenheim and Webster at the National Institute for Medical Research, and concurrently by Windaus in Göttingen. A team of workers at the National Institute, led by Dr. R. B. Bourdillon, appear now to have arrived at the next stage, of isolating the vitamin itself, in crystalline form, from the mixed products of irradiation ; and Professor Windaus, following with his co-workers a different route, has again arrived simultaneously at the same goal. There is no doubt that the substance which the British group now term " calciferol," and which they have isolated as a dinitrobenzoate from the mixed product, is identical with the " Vitamin D_2 " which Windaus and Linsert have obtained by a different method ; and there is little doubt that this substance, as obtained in either laboratory, is the essential vitamin D in a state of practical purity. It appears to be an isomer of ergosterol. One milligramme of calciferol has an antirachitic activity corresponding to about 40,000 of the newly accepted international units.

Such progress in the chemistry of vitamins cannot but be highly satisfactory to all those (and their name is now legion) who have been engaged upon the

Paper by E. N. da C. Andrade

On the Circulations Caused by the Vibration of Air in a Tube.

ERRATA.

Plate 10, facing p. 453, figs. 27 and 28, should be reversed, to *read* as follows :—

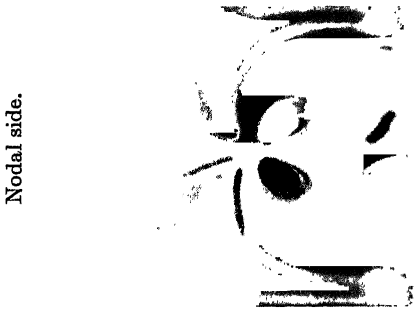

Fig. 27.—Effect of asymmetry in the intensity of the air vibrations, frequency 512.

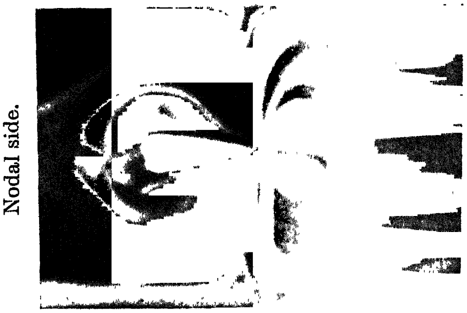

Fig. 28.—Effect of asymmetry in the air vibrations, frequency 1024.

study of their nutritional functions. Our ignorance of their chemistry and the claim that they function in such infinitesimal amounts left, at any rate till recently, in the minds of many who have not been in touch with the evidence some scepticism as to their real importance. Any disbelief in the significance of this field of investigation is, however, fated to disappear, and I venture to predict that in quite other fields discriminative studies of animal nutrition are yet to yield unexpected results of much practical importance.

Before I close I would like to refer for a moment to a certain aspect of the chemical dynamics of living cells, concerning which progressive studies have been made during the last few years. The cell is, of course, a seat of catalysed chemical reactions and would seem to possess a multitude of catalysts each highly specific in the influence it exerts. In the case of reductions and oxidations, however, though these events, like others, are specifically controlled, there are other agencies of less specific activity which promote the final stages of oxidation. Of great interest among these are certain combinations of metallic iron with pyrrol groupings. One such compound is concerned, possibly with the intervention of yet another, in bringing molecular oxygen into the field of activity. What, however, is specially interesting about these associations of pyrrol groupings with a metal is the wide extent of their biological functions. We have long known, of course, of the presence of one such association in the chlorophyll molecule, where it functions as part of the trap for solar energy, and we have been long familiar with the presence of another in hæmoglobin, where its function is to hold oxygen during its transference from the lungs of vertebrates to their tissues. Further, we now know that, within the tissues, two others promote oxidation, and yet a third prevents by its presence any deleterious accumulations of hydrogen peroxide. For adjustment to each separate function there is some slight modification of a fundamental structure. Compounds of the type in question are found in many of the lower organisms, and I am here led to refer to what was said earlier when nerve activity was under discussion. Just as Nature seems to have hit upon sound principles for nerve structure early in evolution, so she seems to have satisfactorily chosen, very early, the chemical materials for life. This same suggestion is carried by all the more important constituents of living stuff; fundamentally the same throughout, yet always with minor differences underlying specific morphological differences. Each of these aspects, the likeness and the unlikeness, has its own interest.

To return to cell dynamics. Knowledge of enzymic catalysts which, with highly specific relations, activate in a certain sense the molecules which are to suffer oxidation, is almost daily accumulating. It is because this specific activation must precede oxidation that the indiscriminate action of oxygen on the living cell is prevented. Although an understanding of the complex organisation of chemical events in the living unit is far beyond our present powers we are, I think, beginning to see what kind of organisation it may be.

One last word, however. We have assumed that the living cells, the units we have best known, are the ultimate units in biology. But of late years the Viruses have forced themselves into our thoughts. Potent agencies, responsible for fell diseases ; small enough to be outside the range of ordinary microscopic vision, yet in some limited sense at least, capable of self-reproduction. What are Viruses ? Do they merely simulate some of the properties of the living ? Can we conceive of them as something between the non-living and the living ? Are they alive ? We do not yet know. Research upon them is at any rate intensely active at the moment. Its results may make it necessary to modify some fundamental biological concepts, and indeed be as revolutionary in its effects as the breaking up of the atom.

Statement of Award of Medals, 1931.

The Copley Medal is awarded to Sir Arthur Schuster.

Sir Arthur Schuster was the first to show the important information to be got by measuring quantitatively the magnetic deflection of cathode rays. He showed how, by combining this measurement with the potential difference which generates the rays, it was theoretically possible to determine without ambiguity the velocity, and the ratio of charge to mass, of the particles constituting the corpuscular stream. The theory of the method, as he laid it down, is exactly that which has stood the test of time. He was less successful in his own experiments in the application of it mainly owing to having attached too much importance to the possible action of residual gas in depriving the particles of their full velocity. Nevertheless the steps he took were a fundamental contribution to the line of work which afterwards led to the discovery of the electron.

We owe to him other almost equally fundamental contributions to the study of electric discharge in gases. Thus, he showed that the passage of a luminous discharge put the gas temporarily into a conducting state, due to the presence of charged ions : these ions were able to diffuse into a space screened from the discharge by a wire gauze partition, and they could then be put into evidence by showing the conductivity of the gas under electromotive forces of a fraction of a volt. The importance of work like this at a time when ionising radiations were still unknown needs no emphasis.

Schuster was the first to show by experiment that in Crookes' radiometer the reaction was not on the sun but on the glass case of the instrument, thereby connecting the action with the residual gas.

He has made many important contributions to terrestrial magnetism. In spectroscopy he formulated independently the Rydberg-Schuster law. He invented the periodogram method of looking for periodicities in statistical material. "The periodogram," he says, "supplies by calculation the transformation which the spectroscope instrumentally impresses on a luminous disturbance." The method has been widely adopted by workers in many branches of enquiry, extending even into economics.

Sir Arthur Schuster's long and valuable services to the Society can never be forgotten.

A Royal Medal is awarded to Sir Richard Glazebrook.

For fifty years Sir Richard Glazebrook has been closely identified with research on physical standards, and particularly electrical standards. For many years he conducted researches associated with the absolute measurement of resistance, current and inductance, and the results of this work, together with his continued interest, is reflected in the present remarkable accuracy of electrical measurements. The name of Sir Richard Glazebrook is also world-known on account of his Directorship of the National Physical Laboratory, in the organisation and development of which he was from the first the active leader; it is largely due to his influence on the researches at that Institution that aeronautical science has made such vast progress. Physical science is also indebted to him for that great work, the "Dictionary of Physics," and in international science he has played a conspicuous part.

A Royal Medal is awarded to Professor William Henry Lang.

Dr. Lang's work on the fossils of the Old Red Sandstone is of high scientific importance. It has led to the discovery and description of a new and unexpected group of plants in which root, stem, and leaf are not differentiated. For the first time it thus becomes possible to trace in a circumscribed group the probable origin of these structures from a source in which they did not exist as distinct members.

The work was begun in collaboration with the late Dr. Kidston, and continued by Professor Lang after the death of his colleague in 1924. Professor Lang's previous intensive studies on the morphology of the Liverworts and

Ferns—in itself a valuable contribution to our knowledge of plant morphology in general, and to the supply of a clearer conception of the interrelationships of the main groups—had eminently fitted him to provide a morphological view-point which has given most important results.

The Davy Medal is awarded to Professor Arthur Lapworth.

Professor Arthur Lapworth's work has been largely concerned with the application of physical methods to the investigation of the reactions of organic chemistry. His researches are distinguished by the simplicity and elegance of the experimental methods which he has employed, and by the insight which he has shown in elucidating the mechanism of chemical change in carbon compounds. His investigations have contributed notably to the deeper understanding of the processes concerned in the chemical reactions of organic compounds.

His study of the bromination of acetone yielded results of primary importance in relation to the reactivity of carbonyl compounds and has formed the basis of many subsequent investigations.

His researches on the addition of hydrocyanic acid to organic compounds, besides leading to results of theoretical and synthetical importance, made clear the mechanism of the formation of cyanhydrins.

His investigations of the effect of small quantities of water in diminishing the activity of acids in alcoholic solution indicated the existence of the oxonium ion, and added considerably to our knowledge of catalysis by acids.

Among his more notable synthetical achievements are the synthesis of zingerone, derived from the pungent principle of ginger, and of homocamphor.

His work on the mutual influence of groups in the same molecule, his recognition of induced alternate polarity, and his classification of reagents as anionoid or kationoid have played an important part in the development of the present state of knowledge of the reactivity of organic compounds.

The Sylvester Medal is awarded to Professor Edmund Taylor Whittaker.

Professor E. T. Whittaker is one of the best known of British mathematicians, his work showing extraordinary versatility. He has written five books, on entirely different subjects, and some 50–60 papers which touch on almost every branch of mathematics. His book " Modern Analysis " (now Whittaker and Watson) is a standard treatise in its 5th edition; his " Analytical Dynamics " and his tract on " Optical Instruments " have both been translated into German; and he has also written a " History of the Theories of Aether and Electricity," and a " Calculus of Observations." All these works show, besides their more technical qualities, powers of arrangement and exposition of a most unusual order; and the "Modern Analysis" in this country, and the "Analytical Dynamics" both in this country and abroad, have had a considerable influence on mathematical thought.

It is only possible to mention a few of Whittaker's original contributions to knowledge (beyond the considerable number absorbed in his books). He has made important additions to the theory of the solution of differential equations, ordinary and partial, by definite integrals; to the theory of Lamé and Mathieu functions, the functions of the elliptic and parabolic cylinders, and the integral equations associated with them; to the theory of interpolation; and to the theory of the solution of dynamical problems by trigonometrical series. He has also in recent years made a number of interesting contributions to the pure mathematics of relativity, electromagnetism and quantum theory.

The Hughes Medal is awarded to Professor William Lawrence Bragg.

Professor W. L. Bragg's recognition of the fact that the Laue diffraction spectra could be considered as produced by reflection from the planes of the crystal lattice, besides being a great simplification of a difficult geometrical problem, was the starting-point of two important and fruitful lines of physical investigation, namely, the measurement of X-ray wave-lengths and the elucidation of crystal structure. Work on the first of these led to Moseley's discoveries and their subsequent developments. Bragg's concentration on the second has resulted in a wonderful extension of our knowledge of the structure of crystals, both simple and complex, and of inter-atomic distances and linkages. His work may truly be said to have laid the foundations of a chemistry of the solid state.

The Sorption of Carbon Bisulphide at Low Pressures by Activated Charcoals.

By A. J. Allmand, F.R.S., and J. L. Lizius, King's College, London.

(Received October 27, 1931.)

1. *Introductory.*

Results of measurements carried out in this laboratory on the adsorption of CCl_4 vapour by charcoal at low pressures have recently been published. It was considered desirable to carry out similar measurements with another vapour and, in particular, to investigate two points, viz. (1) whether the heat of sorption rose steadily as the charge on the charcoal decreased, or whether it remained constant over a certain range of concentration, only rising further at quite low charges, as was found* with CCl_4 when using charcoals degassed at 110°, and (2) whether "breaks" occurred in the isosteres, as was found† with CCl_4, and as has since been confirmed,‡ in the case of many isothermals, by using other experimental methods.

The new sorbate was CS_2, the choice largely being determined by the wish to carry out subsequent experiments with mixtures of aqueous vapour and a second sorbate, CS_2 offering certain advantages over CCl_4 in this connection. The A.R. specimen was redistilled before use.

Six charcoals were investigated, viz. A,§ B,§ and C,§ already employed in the work on CCl_4, and charcoals H,|| K,¶ and L,¶ Of these materials, A, B and L are made from birch-, pine- and beech-wood respectively, C from coconut, H from a coconut-coal mixture and K from peat; whilst A is air-activated, C, H and L steam-activated, and B and K chemically activated (by zinc chloride and phosphoric acid respectively). In every case the granules used were graded by the aid of 10-mesh and 12-mesh sieves, whilst** the charcoals were all degassed beforehand in the usual manner at 110° C., until the gas pressure at that temperature had fallen to about 2×10^{-4} mm.

Work was confined to the investigation of the isosteres,** a number of which were determined for each specimen of charcoal. The isothermals at 25° C.

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* Allmand and Chaplin, 'Proc. Roy. Soc.,' A, vol. 129, p. 256 (1930); quoted hereafter as A. and C.

† A. and C., p. 257.

‡ Allmand and Burrage, 'Proc. Roy. Soc.,' A, vol. 130, p. 610 (1930).

§ 'J. Phys. Chem.,' vol. 32, p. 441 (1928).

|| 'J. Soc. Chem. Ind.,' vol. 47, p. 372T (1928).

¶ 'J. Phys. Chem.,' vol. 34, p. 2202 (1930).

** Except for the experiment with charcoal A described in Section 5.

have, however, been computed from the isostere data, and some interesting points have arisen.

2. *Apparatus and Procedure.*

These were essentially as designed and worked out on CCl_4,* but with certain modifications.

Carbon Bisulphide Supply.—Instead of using a liquid supply, S† was replaced by a bulb which could be shut off by a tap, containing charcoal charged with CS_2.

Initial Charging Process.—Carbon bisulphide, just like CCl_4, displaces the residual oxygen charge on a charcoal in the form of CO and CO_2. In every case the charcoal under test was saturated with CS_2 from S at a pressure of about 0·3 mm., the container being then immersed in a water-bath at 80° to 100° for an hour whilst the displaced gases were removed by the pumps. In order to test whether this elimination of gases was complete, a charge was taken out of the charcoal, liquid oxygen (—183°) placed on the freezer F_1, and permanent gas pumped off. Any condensed CO_2 was then removed by replacing the liquid oxygen by melting methylcyclohexane (—126·3°), and again opening to the pumps. This operation was repeated until successive readings on the gauge, with F_1 alternately at —183° and at —126·3°, were constant, showing CO_2 to have been eliminated from the system as far as possible. A similar procedure was adopted when determining sorption points.

Desorption Process.—Liquid oxygen was placed on F_1, the tap of the container C opened (if necessary, C was immersed in hot water), the condensed CS_2 freed from permanent gas and CO_2 as above, and then taken back into S by immersing the latter in liquid oxygen.

Calibration of the Gauge.—For this purpose, direct measurements were made with a mercury U-manometer of the saturated vapour pressures of CS_2 between —45·2° C. and —111·6° C., its freezing point. The plot of $\log p$ against T^{-1} is a straight line. These pressures between —83·6° and —126·3° are such that the corresponding voltage readings could be measured on the Pirani gauge. Again, the plot of the logarithm of the voltage function against T^{-1} is a straight line. The two straight lines are parallel; hence a comparison of the pressure and voltage function values for the same temperature gives the gauge coefficient α which, like that for CCl_4, is constant over a large range of pressure.

The results of the measurements are contained in Tables I and II and plotted in fig. 1.

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* Chaplin, 'Proc. Roy. Soc.,' A, vol. 121, p. 344 (1928); also A. and C., p. 252.

† This and similar references are to Chaplin, *loc. cit.*, fig. 2.

Table I.

Refrigerant.	Melting point.	T^{-1}.	p.	$\log_{10} p$.
	° C.		mm.	
Chlorobenzene	−45·2	0·004390	11·86	1·015
Ethyl malonate	−50·0	4480	7·39	0·869
Chloroform	−63·5	4773	2·58	0·412
Solid carbon dioxide	−78·0	5125	0·69	$\bar{1}$·84
Ethyl acetate	−83·6	5279	0·40	$\bar{1}$·60
Toluene	−94·6	5602	0·12	$\bar{1}$·08
Carbon bisulphide	−111·6	6195	0·01	$\bar{2}$·00

Table II.

Refrigerant.	Melting point.	T^{-1}.	$f(v)$.	$\log_{10} f(v)$.
	° C.			
Ethyl acetate	− 83·6	0·005279	5·546	0·744
Toluene	− 94·6	5602	2·065	0·315
Ethyl alcohol	−112·3	6221	0·195	$\bar{1}$·29
Allyl bromide	−119·4	6511	0·0676	$\bar{2}$·83
Unstable ether	−123·3	6678	0·0407	$\bar{2}$·61
Methylcyclohexane	−126·3	6816	0·021	$\bar{2}$·32

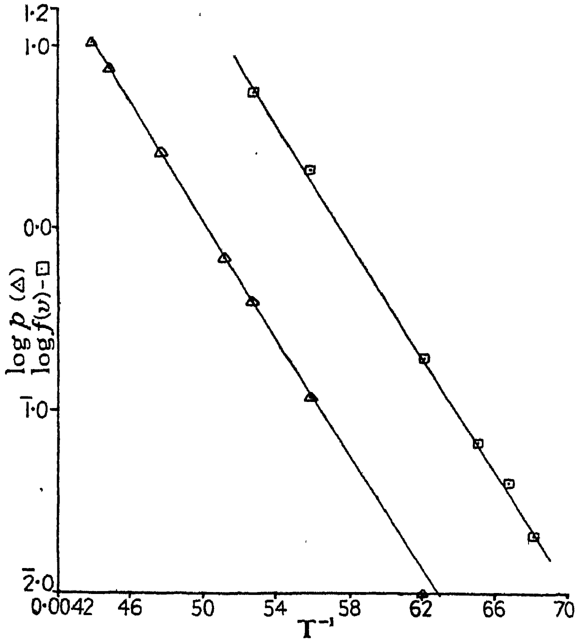

Fig. 1.

The error in the cathetometer readings did not exceed 0·01 mm. The vapour pressure value at —111·6°, although not on the curve as drawn, in reality lies on it within the experimental error (0·013 mm. for 0·01 mm. would put the point on the curve).

We have

$$p = \alpha \frac{v^2 - {v_0}^2}{{v_0}^2} = \alpha f(v),$$

where v is the voltage reading with the pressure p and v_0 is the gauge zero, whence

$$\log \alpha = \log p - \log f(v).$$

From the two straight lines in fig. 1, $\log \alpha$ is $\bar{2}\cdot822$ and α is $0\cdot0664$.

Measurement of Partial Pressures in Gaseous Mixtures.—It was necessary to measure pressures due to permanent gas, CO_2 and CS_2. The two latter were first frozen out by means of liquid oxygen on the freezer F_1. The permanent gas pressure was then measured, and the gas removed by exposing the working space to the charcoal in P at —183°. There is no refrigerant that will completely separate CO_2 and CS_2, but the vapour pressure of the latter is very low (0·0014 mm.) at the temperature of melting methylcyclohexane (—126·3°). Hence, on immersing F_1 in this refrigerant, the pressure measured was almost entirely due to CO_2, which could then be removed by opening up to the charcoal in P *for a time depending on the quantity of the gas present.* A procedure of this kind was essential, because with only a small quantity of CO_2, exposure of the apparatus to the charcoal in P for even a few minutes removed some CS_2, in spite of its low vapour pressure at —126°, and this led to low results for its pressure when subsequently measured.

Fig. 2, determined by special experiments, shows the relation found between the initial Pirani gauge reading $v - v_0$, with F_1 at —126·3°, and the time found necessary for the CO_2 to be cleaned up by the charcoal in P (—183°) when the apparatus was put into connection with the latter. The fact that the curve does not pass through the origin is due to the small residual CS_2 pressure at —126·3° already referred to.

After removal of the CO_2 and having shut off P, the pressure due to CS_2 was obtained by allowing F_1 to warm up to room temperature.

An example of an actual determination of partial pressures will make the procedure clear :—

(i) Charcoal in container already charged. Thorough evacuation of the apparatus and 18 hours of clean-up with charcoal in P at —183°.

$$v_0 = 4\cdot355 \text{ volts (gauge zero).}$$

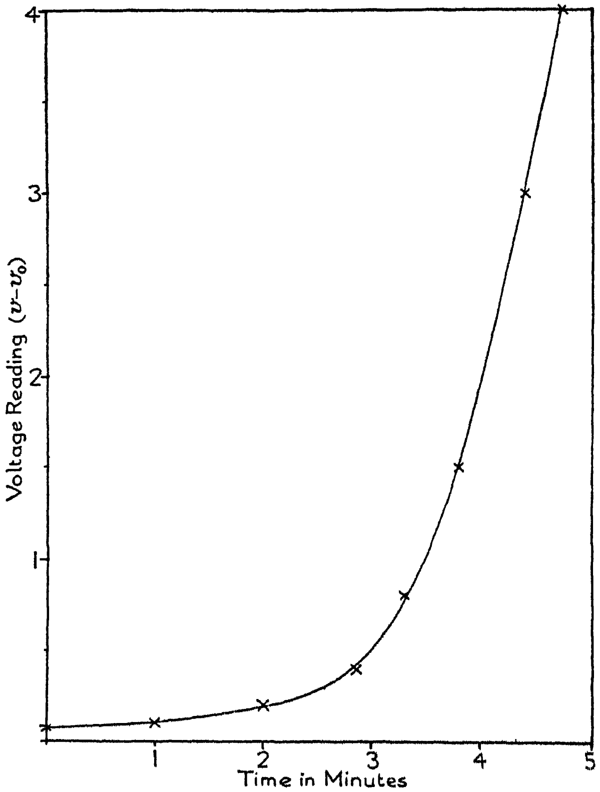

FIG. 2.

(ii) Shut off P. Charge of vapour taken from the charcoal F_1 at room temperature.

$v = 6 \cdot 10$ volts.

$f(v) = 0 \cdot 961$ (permanent gas, CO_2 and CS_2).

(iii) F_1 immersed in liquid oxygen (—183°).

$v = 4 \cdot 395$ volts.

$f(v) = 0 \cdot 018 - 0 \cdot 019$ (permanent gas only).

(iv) Permanent gas removed by 5 minutes' exposure to P at —183°. F_1 at —183°.

$v = 4 \cdot 355$ volts $= v_0$ (gauge zero).

(v) P sealed off from apparatus. CO_2 vapourised by replacing liquid oxygen on F_1 by melting methylcyclohexane (—126°).

$v = 4 \cdot 70$ volts, *i.e.* $v - v_0 = 0 \cdot 345$ volt,

corresponding to just over $2\frac{1}{2}$ minutes in fig. 2.

(vi) Apparatus opened up to P (—183°) for just over 2½ minutes. P sealed off.

$$v = 4 \cdot 435 \text{ volts},$$

which, combined with the v value in (v) gave $f(v) = 0 \cdot 123$ (CO_2 only).

(vii) Methylcyclohexane removed and F_1 allowed to attain room temperature.

$$v = 5 \cdot 855 \text{ volts and } f(v) = 0 \cdot 808 \ (CS_2 \text{ only}).$$

Hence

$$\log p = \bar{2} \cdot 729 \text{ and } p_{CS_2} = 0 \cdot 0536 \text{ mm.}$$

At the beginning of these experiments, $f(v)$ for CS_2 was obtained by subtracting the sum of the $f(v)$ values for CO_2 and permanent gas from the total voltage function, a procedure similar to that employed during the work with CCl_4 already published. Thus, in the example given, $f(v)$ for CS_2 would be $0 \cdot 961 - 0 \cdot 019 - 0 \cdot 123 = 0 \cdot 819$. The values obtained by this method are indeed fair approximations, except in the presence of a quantity of CO_2 comparable with that of the CS_2 present. The procedure, however, is incorrect in principle, as it tacitly assumes that the Pirani gauge α coefficients are the same for CO_2 and CS_2, which is not the case. Indeed, it was found in practice, when determining the vapour pressures of CS_2 over a series of temperatures in presence of traces of CO_2 and permanent gas, that the log p values obtained by the method of difference just outlined, when plotted against T^{-1}, did not fall exactly on a straight line. For this reason, it was decided to adopt the method described above of (*a*) removing permanent gas and CO_2, and (*b*) vapourising the residual CS_2 and measuring its pressure directly.

It may be mentioned at this point that one rather unexpected feature of our experiments was the liberation of amounts of CO_2 far higher than those normally observed when working with CCl_4. Whereas in the determination of the separate points of the CCl_4 isosteres of charcoal B, the CO_2 pressures developed were usually of the order of $0 \cdot 5 \times 10^{-4}$ mm., and rarely reached $0 \cdot 5 \times 10^{-3}$ mm., in the present work both average and exceptional pressures were at least 10 times as great. Similarly, with charcoal C, the figures, higher in both sets of experiments than with B, averaged about 1×10^{-3} mm. with CCl_4 and 6×10^{-3} mm. with CS_2. But, as will be seen, this continued evolution of CO_2, naturally more marked at relatively high temperatures, was not accompanied by drift or irreversibility, as in the CCl_4 experiments when comparable quantities of gas were being displaced.

3. *Isosteres.*

In every case, the first isostere was determined for a charcoal containing a relatively high charge of CS_2, and was followed by a series of isosteres for less heavily charged charcoals (*desorption isosteres*). When the lowest q value had been reached, the charcoal was recharged to a higher CS_2 content, and one or more *resorption isosteres* measured. In the case of charcoal B, the whole sequence was repeated, the results therefore including two sets each of desorption and of resorption isosteres.

The average of points on each isostere was about six. The results were plotted in the form of $\log p$ against T^{-1}, and, from the slopes of the resulting linear graph,* the molecular heat of adsorption (λ) was calculated. Whenever pressures above 0·1 mm. or thereabouts were measured, the isosteres were found to exhibit "breaks," the slopes of the curves at higher pressures corresponding to lower values of λ, just as was the case with the isosteres of charcoals charged with CCl_4.

The results are summarised in Table III, the data being given in the order in which they were determined. The third column contains the values for λ at pressures below the discontinuity, the fourth column the pressures at which the discontinuities were observed, and the last column λ' values for pressures immediately above the break. The figures for q are in milligrams per gram, those for λ in Calories per molecule, and p values in millimetres of mercury. The error in the values of λ we estimate as not exceeding 0·2 cal./mol. It is greater for the λ' figures, as their evaluation usually depends on two isostere points only.

The values of λ are plotted against q in fig. 3 (circles and triangles) numbered in the order of their determination, and several points call for remark. The first is the absence in the curves of any horizontal portion, denoting a constancy of λ over a certain q range, such as was found with CCl_4. It is quite possible that, in the case of charcoal L, λ may indeed be constant over a considerable q range, and the slopes of the curves for A and C appear definitely to be less in the intermediate q region than at higher and lower charges of CS_2. But, in general, the introduction of horizontal sections into the curves would be unjustified.

The second fact to notice is that, as any one of the experiments proceeds, the heat of adsorption at a given CS_2 charge tends to become smaller. The effect is not very marked with A, H and K, but in these cases one resorption

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* Similar to those in A. and C., fig. 1, p. 253.

Table III.

Charcoal.	q.	λ.	p.	λ'.
	mg./g.	Cals./mol.	mm.	Cals./mol.
A	71·5	11·6	0·105	9·6
	47·7	12·3	0·10	10·4
	25·0	12·7	0·107	10·0
	14·4	13·5	—	—
	7·7	15·1	—	—
	12·3	13·7	—	—
B	11·1	12·9	0·10	9·1
	4·6	13·0	—	—
	1·3	13·5	—	—
	0·7	15·3	—	—
	9·8	12·3	0·10	9·1
	24·3	11·0	0·10	9·0
	15·7	11·5	0·10	9·3
	11·6	11·75	0·10	9·3
	5·5	12·3	0·10	10·0
	0·9	14·4	—	—
	8·1	11·9	0·10	9·7
	14·0	11·5	0·10	9·3
	23·5	10·8	0·10	9·2
C	57·1	11·5	0·126	8·6
	40·3	12·1	0·105	9·2
	25·5	12·4	0·10	10·3
	8·1	13·5	—	—
	5·0	14·4	—	—
	6·5	13·6	—	—
	15·4	12·4	—	—
	32·9	12·0	0·10	9·6
	60·2	11·1	0·144	8·6
H	56·5	11·6	0·129	8·7
	38·0	12·0	0·115	9·3
	18·7	12·6	0·107	10·7
	6·2	14·8	—	—
	16·4	12·7	0·10	10·5
K	41·6	10·8	0·12	8·1
	28·7	11·1	0·10	9·1
	14·5	11·7	0·10	10·2
	3·7	13·5	—	—
	1·5	15·7	—	—
	7·3	12·35	0·10	10·3
L	73·5	11·8	0·10	—
	47·8	11·9	0·10	9·6
	26·2	12·3	0·102	9·4
	14·0	14·0	0·102	—
	5·1	16·0	—	—
	10·5	13·5	—	—
	28·5	11·8	0·105	9·5
	74·4	11·6	0·10	8·9

isostere only was determined. In the case of charcoal B, which was investigated more fully than the others, this self-poisoning effect was just as pronounced during the second desorption and second resorption as during the first resorption.

Nothing of the kind was noticed with CCl_4, where the λ/q curves, for " 110° C." charcoals, were reversible within experimental error. After some of the experiments, the charcoal was noticed to have acquired an unpleasant smell not shown by the original CS_2 used, and, although we cannot definitely correlate

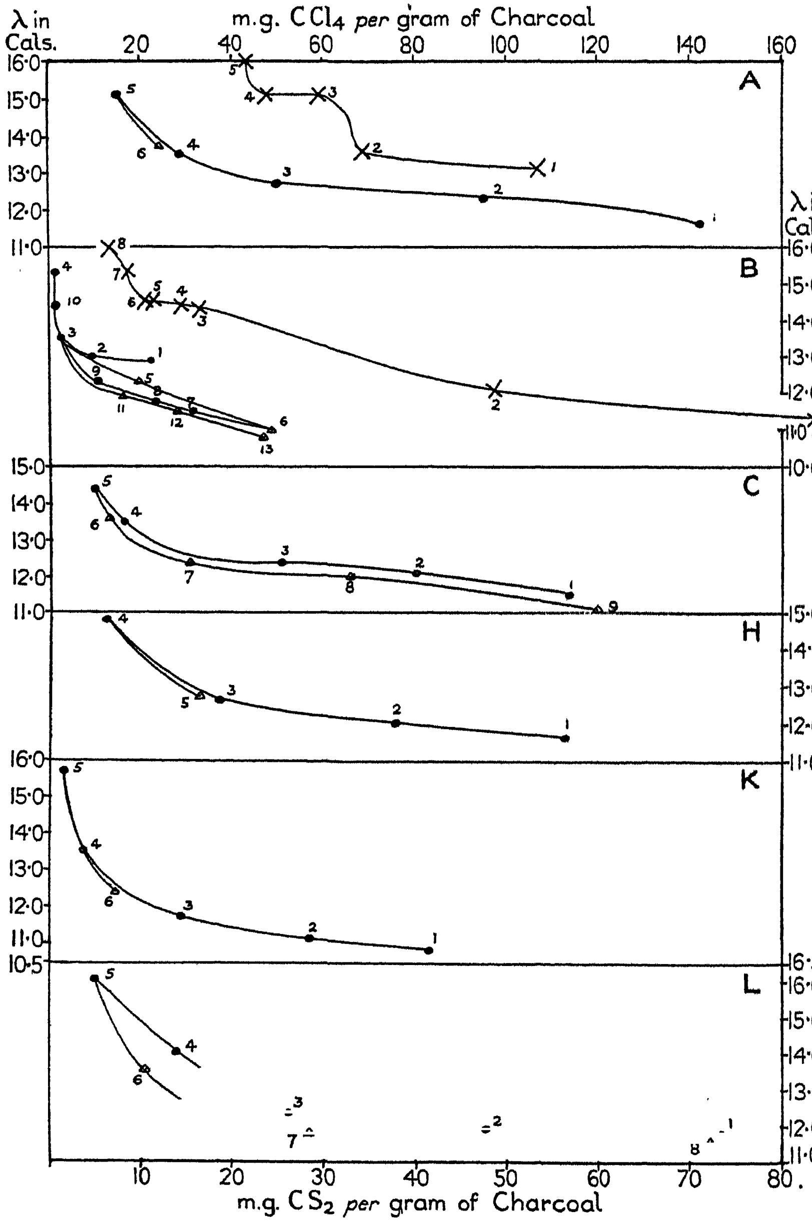

FIG. 3.

this fact with the self-poisoning effect, it is possible that the two phenomena are connected.

The third point concerns the relative values of λ found with the different charcoals at identical values of *q*. Owing to the irreversibility just mentioned, no exact comparison can be made. But, considering the whole range of *q*, it is clear that A and L, both soft-wood charcoals, air- and steam-activated respectively, give the highest values of λ, that the two steam-activated charcoals C and H are similar to one another, but give lower values than do A and L, and that the two chemically activated charcoals B and K are characterised by definitely lower heats of adsorption than the other charcoals.

Finally, it is of interest to compare the λ values obtained for A, B and C with those given by the same charcoals with CCl_4. As the molecular weights of CS_2 and CCl_4 are nearly in the ratio of 1 : 2, it would seem best to compare the heats of sorption of CS_2 at a *q* value of, say, 20 mg./g. with the values for CCl_4 given by charcoals holding 40 mg./g. taken from the data of Allmand and Chaplin. If this be done, then we obtain the (approximate) figures given in Table IV.

The order of the charcoals in the two cases is seen to be the same, whilst λ_{CCl_4} is definitely higher than λ_{CS_2} for charges of the same average molecular density.

Table IV.

Charcoal.	λ for CS_2 at $q = 20$ mg./g.	λ for CCl_4 at $q = 40$ mg./g.
A	12·9 Cals. (average)	15·9 Cals.
C	12·4 Cals. (average)	14·6 Cals. (at least)
B	11·2 Cals. (average)	14·0 Cals.

In view of the fact that the horizontal sections on the λ/*q* curves found with CCl_4 were not given by CS_2, it seemed desirable to determine a few fresh isosteres with CCl_4—charged charcoals, using the modified technique, *i.e.*, directly measuring the CCl_4 pressures instead of obtaining them by difference. Such experiments were done with charcoals A and B previously outgassed at 110° C., the CCl_4 present in any equilibrium vapour sample (after removal of permanent gas) being frozen out at —112·3° by melting ethyl alcohol, the CO_2 removed in the usual way, the CCl_4 revapourised and its pressure determined. The calculated λ values are shown in fig. 3 (crosses—the *q* scale is halved compared with that for CS_2). It may be added that "breaks" were observed on the isosteres at pressures varying between 0·076 and 0·099 mm. with charcoal A and 0·091 and 0·135 mm. with charcoal B.

Although the number of points is insufficient to define the curves with any precision, there are in both cases definite indications of the existence of the halts previously noticed. With A, the corresponding λ value is about 0·5 Cal. above the figure previously found, whilst with B the old and new values are practically the same within the experimental error. The q ranges over which the halts are found are much as before. It thus appears that their existence does not depend on any error in the pressure measurements,* and that the suggestion already made,† viz., that the halts are "associated with an active charcoal surface still poisoned by a certain amount of tenaciously held oxygen" is probably correct. It must, however, now be concluded that the actual λ values at which such halts occur themselves depend on the exact state of the surface.

4. *Isothermals at* 25° *C.*

As was done in the case of CCl_4,‡ isothermals for 25° have been "derived" from the isosteres of the different charcoals, and are plotted logarithmically in fig. 4, the points being numbered in the order of their determination. Whilst the data are not all of the highest accuracy, they present several features of interest:—

(*a*) The curves show no sign of the drift observed in the case of CCl_4 with both directly determined and derived isothermals. On the contrary, the resorption curves tend to exhibit pressures higher than those of the desorption curves, a type of behaviour only noticed with CCl_4 when working with charcoal D§ outgassed at 110°, and then ascribed to delayed displacement of adsorbed CO_2 from the charcoal surface. In the present case, the drift of the isothermals towards higher pressures has its analogue in the drift of the heats of adsorption towards lower values already discussed, the parallelism being a complete one, and the cause (suggested above as a self-poisoning of the charcoal due to the formation of some product of reaction or decomposition of the CS_2) being clearly the same in the two cases. The absence of the more usual type of drift is remarkable when the continued evolution of CO_2 during the

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* Systematic calculations applied to the present results showed that the approximate method of measuring CCl_4 pressures used by Allmand and Chaplin introduced important errors only when these pressures themselves are very low.

† A. and C., p. 265.

‡ A. and C., p. 248.

§ A. and C., p. 241.

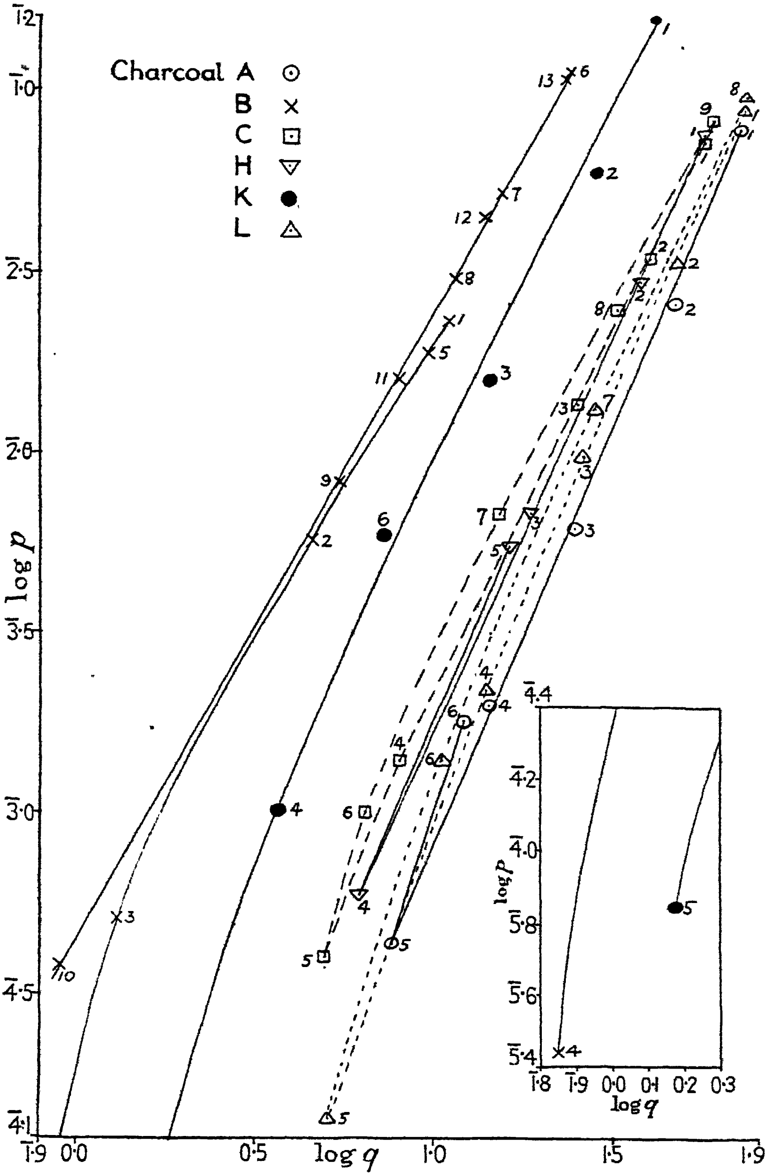

FIG. 4.

experiments, and the behaviour of charcoal-CCl_4 systems under similar conditions, are considered.

(*b*) It will be noticed that a sudden rise in the λ/q curves of fig. 3 corresponds to an isothermal in fig. 4 which is concave to the log q axis in that region. A linear isothermal (Freundlich equation), or one slightly curved, corresponds to a linear, or almost linear, λ/q curve.

(*c*) The isothermals group themselves in a similar fashion to the λ/q curves, although the parallelism is not complete in detail. Nevertheless, charcoals A and L lie at the highest q/p ratios, followed closely by C and H, whilst B and K have considerably lower sorptive powers under these low pressure conditions.

(*d*) The relative positions of the isothermals for charcoals A, B and C are different from those of the CCl_4 isothermals* for the same charcoals (outgassed at 110°). Whereas the q values at a pressure of 2×10^{-2} mm. of CS_2 are about 43, 10 and 30 mg./g. for charcoals A, B and C respectively, the corresponding figures at the same relative pressure of CCl_4, say, 7×10^{-3} mm., are approximately 60, 40 and 130 mg./g. for the same series of charcoals. Thus, at this relative pressure, C is about three times as effective a sorbent as B both for CCl_4 and for CS_2, whilst charcoal A, which is far inferior to charcoal C in respect of CCl_4, is the better sorbent for CS_2.

5. *Isothermal of Charcoal A degassed at* 800° *C.*

It was realised, during the course of the experiments with CCl_4 and " 110° C." charcoals, that at all events charcoal A, in consequence of the slow elimination of adsorbed gas from its surface, was exerting much less than its maximum adsorptive capacity, and that this was true to a lesser extent of C, and also possibly of B. Further work† has shown that, whilst degassing at 800° increases the sorptive capacity of charcoal C to a comparatively small extent, the effect on A is far greater, and experiments were done which indicated that this increased capacity is due to the removal, as oxides of carbon, of adsorbed oxygen from the surface.

Those results, together with the facts mentioned in Section 4 (*d*), as also the absence of drift when working with CS_2, suggested to us that this substance may be a far more powerful agent for the displacement of tenaciously absorbed oxygen than is CCl_4. Whilst the latter only slowly removes oxygen from charcoal A, even after degassing at 800°, this displacement is rapidly effected by

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* A. and C., fig. 7, p. 250.

† Allmand and Puttick, 'Proc. Roy. Soc.,' A, vol. 130, p. 197 (1930).

CS_2, even after merely degassing at 110°. The necessary consequence of this hypothesis would be that, contrary to what happens with CCl_4, the raising of the outgassing temperature to 800° should not result in any particular increase in adsorptive capacity towards CS_2; and further, there should, of course, be no drift.

We accordingly determined the CS_2 isothermal at 25° on a specimen of charcoal A, previously degassed in the usual manner at 800°. In order to give every opportunity for effective gas displacement, the degassed charcoal was first charged with CS_2 at about 0·3 mm. pressure, and the container kept overnight at 100°. After cooling to 25°, the displaced gases were removed, and 10 desorption points determined (point 1, 113·9 mg./g. and 0·193 mm.; point 10, 10·6 mg./g. and 0·00073 mm.). These were followed by seven resorption points, point 17 (113·3 mg./g. and 0·193 mm.) being practically identical with point 1. The charcoal was then recharged at a pressure of 0·5 mm., the container kept at 100° for an hour, cooled, and the displaced gases removed. A second series of 13 desorption points was measured (point 18, 170·9 mg./g. and 0·457 mm.; point 30, 13·0 mg./g. and 0·0011 mm.), and, finally, a second short series of resorption points (point 34, 83·3 mg./g. and 0·0867 mm.).

During the whole experiment there was a small pressure of permanent gas present in the gas samples analysed, varying somewhat irregularly, and averaging $2 - 3 \times 10^{-4}$ mm. The initial CO_2 pressure was of the same order, and disappeared entirely during the first desorption series. It reappeared with point 12 and rapidly increased, amounting to 5×10^{-3} mm. at point 18. During the second desorption, it again fell to zero, but small quantities of the gas were present during the final resorption measurements.

The results are plotted logarithmically in fig. 5. There is no trace of drift, the isothermal differing in this respect very remarkably from the corresponding CCl_4 curve. On the contrary, the first resorption curve shows the apparent self-poisoning found in the isothermals for the "110° C." charcoals. This is barely perceptible (point 31) in the second resorption series; in fact, the points of this series and all the desorption points fall satisfactorily on a reversible curve, which is linear up to about 3×10^{-2} mm., then becomes slightly concave to the log p axis, and shows discontinuities above 0·1 mm., the number of points, however, being insufficient to define exactly the position of the "breaks."

Finally, the actual data are very similar to those given by the "110° C.' charcoal, as is shown by Table V.

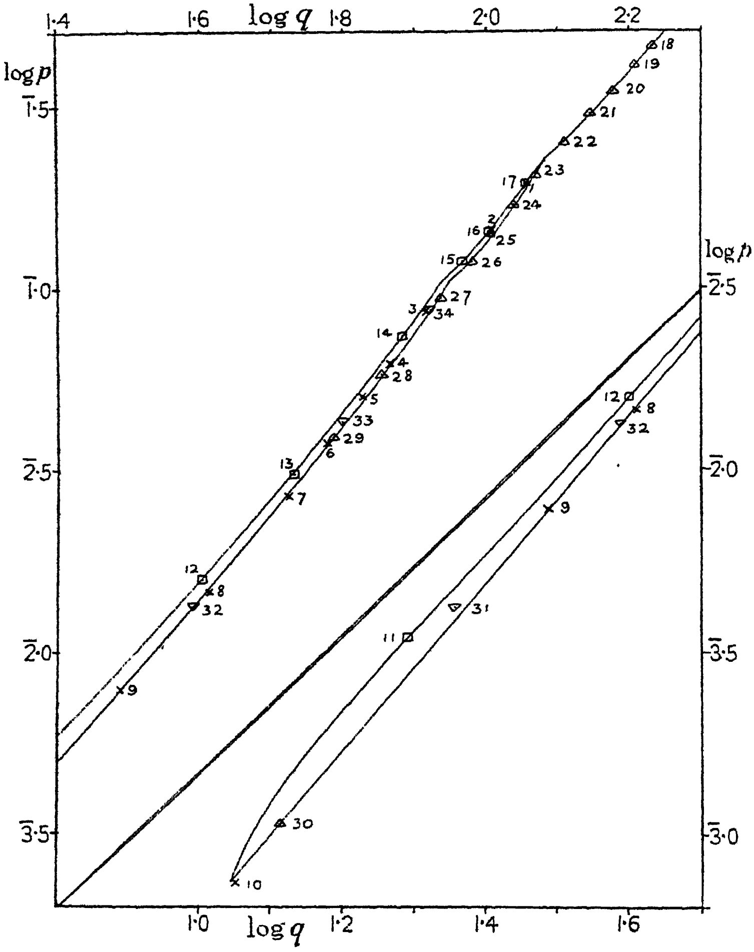

Fig. 5.

Table V.

$\log_{10} p$. (in mm.).	q in mg./gram.	
	110° C. charcoal.	800° C. charcoal.
$\bar{3}\cdot0$	10·8	12·7
$\bar{3}\cdot5$	17·8	20·9
$\bar{2}\cdot0$	30·2	34·4
$\bar{2}\cdot3$	40·7	46·4
$\bar{2}\cdot5$	50·1	56·9
$\bar{1}\cdot0$	79·4	87·7

The maximum figures observed for CCl_4 at $\log p = \bar{2}\cdot 3$ were about 87 mg./g. or q_{110} and 138 mg./g. for q_{800}.

6. *Discussion.*

The results quoted in the last section appear to support our hypothesis that CS_2 is more effective in breaking up the carbon-oxygen complex, the existence of which we postulate on the surface of active charcoals, than is CCl_4. On the other hand, the heat of adsorption of CCl_4 exceeds that for CS_2 under comparable conditions, and it might be expected that displacing action and heat of adsorption should show a certain parallelism. In this connection, however, it must be remembered that, in the experiments with CS_2, relatively large amounts of CO_2 were being continually evolved from the charcoal surface, their liberation not being accompanied by " drift," as was the case with CCl_4.

This being so, we feel justified in attempting to distinguish two stages in the elimination of the residual oxygen charge from the charcoal,* viz. (*a*) the conversion of the surface complex into truly adsorbed CO_2 (or CO) and (*b*) the displacement of this adsorbed gas from the surface. Stage (*a*) we imagine to be effected rapidly by CS_2 and slowly by CCl_4. It is the process which is responsible for " drift " in experiments with the latter substance and, when once it has taken place, the charcoal surface is possessed of its maximum adsorptive capacity. Stage (*b*), on the other hand, takes place more rapidly with CCl_4 than with CS_2, in accordance with the higher heat of adsorption of the former. It is a process which normally has little effect on the total amount of vapour adsorbed at any given pressure, and hence its slow occurrence does not cause drift.

The position of the points of the first resorption series in the CS_2 isothermal on " 800° C." charcoal (fig. 5, points 11–17), if considered alone, might well be ascribed to delayed displacement of *strongly* adsorbed CO_2,† particularly as the second resorption curve coincides with the two desorption curves, suggesting that no permanent self-poisoning has taken place. On the other hand, it seems difficult to interpret in the same way the corresponding phenomena observed during the measurement of the isosteres on " 110° C." charcoals.

The interesting question of the relative capacities for CS_2 and for CCl_4 of the different charcoals will be discussed elsewhere, in conjunction with further results which have been obtained by the retentivity method.

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* As already mentioned, a distinction between these two stages in the displacement process was suggested in a former paper, A. and C., pp. 246, 263.

† *Cf.* A. and C., p. 264.

Summary.

(1) The results of a number of isostere measurements on six different charcoals, previously degassed at 110° C., and carrying various charges of carbon bisulphide, are communicated, together with the heats of adsorption and isothermals at 25° C. calculated from them.

(2) At pressures below 10^{-1} mm., the heat of adsorption in every case rises continuously as the charge on the charcoal decreases. On subsequent resorption it is found to decrease slightly. In every case, if the pressure exceed 10^{-1} mm., it decreases sharply.

(3) The carbon bisulphide isothermal at 25° C., given by a particular charcoal after degassing at 800° C., has been studied, and found to be reversible in nature, in accordance with prediction.

(4) The mechanism whereby the oxygen charge on a charcoal surface is displaced during the adsorption of a vapour is examined more closely in the light of differences in this respect shown by carbon tetrachloride and carbon bisulphide.

We are indebted to Dr. E. G. V. Barrett for the measurements on carbon tetrachloride described in Section 3.

The Isotopic Constitution and Atomic Weights of Cæsium, Strontium, Lithium, Rubidium, Barium, Scandium and Thallium.

By F. W. Aston, F.R.S.

(Received November 7, 1931.)

Introduction.

The following is an account of further experiments in continuation of those recorded in three previous communications.* After the experiments on chlorine described in the third of these a new discharge bulb was fitted and an attempt was made to get the mass spectrum of tantalum by means of a volatile chlorine compound of this element kindly supplied by Dr. Krishnaswami, of Bangalore. The vapour of this liquid, which was of unknown composition, was introduced into the discharge without difficulty, but gave every appearance of rapid decomposition and even with the most prolonged exposures failed to give any indication of the lines of tantalum.

A similar failure must be recorded with a volatile platinum compound $PtCl_2(CO)_2$ prepared specially for the purpose by Dr. A. v. Grosse. This compound was treated in the same way as was rhenium heptoxide (*loc. cit.*), but gave no platinum lines even when chlorine was introduced.

With a view to measuring the packing fractions of cæsium and barium and so throwing light on the discrepancies between their chemical atomic weights and those suggested by the early results of the mass-spectrograph, an attempt was now made to devise a form of discharge in which "gas rays" (the meaning of this term will be obvious) and anode rays could be produced simultaneously. For this purpose the customary 8-inch bulb was replaced by a 6-inch one which was equipped with a composite anode of the type used in the method of accelerated anode rays.† With the normal arrangement in which the composite anode is placed close to the cathode and well within the Crookes dark space, the gas rays are completely cut off by it from the slit system, making it impossible to register suitable standard lines by which packing fractions can be determined. Costa, in making his measurements of the lithium isotopes, moved the lithium anode out of the way mechanically between exposures, but since in such movements there must be a risk of disturbing the constancy of the fields, some compromise enabling the production of both kinds of rays simultaneously is clearly to be preferred for measurements of high accuracy.

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* 'Proc. Roy. Soc.,' A, vol. 126, p. 511; vol. 130, p. 302; vol. 132, p. 487.

† 'Phil. Mag.,' vol. 47, p. 385 (1924).

After a series of trials it was found that by a suitable setting of the composite anode near the middle of the bulb, the gas rays were sufficiently unobstructed to produce an effect of the same order of intensity as that of the metallic rays arising from the surface of the anode. The intensities of both sorts of rays is poor, as would be expected from such a compromise, but it is adequate for the purpose and by this means the packing fractions of cæsium and barium were determined, as will be described.

Following this work, the normal 8-inch discharge bulb was put back for a preliminary attempt to determine quantitatively the relative abundance of isotopes in leads from various radioactive minerals. A number of samples, in the form of methides, had been obtained for this purpose, but on trying one the very poor results indicated that an improved setting of the apparatus would be necessary before this difficult problem could be hopefully attacked. During this period unprecedented trouble with a small leak was experienced and the mass-spectrograph had to be entirely dismantled before a cure was effected.

On rebuilding it was decided to try the effect of substituting a modern high-speed mercury diffusion pump for the liquid nitrogen cooled charcoal tubes previously used on the low pressure parts of the apparatus. For testing this a Dushman ionisation gauge was attached to the camera. This showed that under normal working conditions with cooled charcoal the pressure in the camera was about 0·1 microbar—about that expected and previously estimated —while the discharge was in action. If the discharge was stopped and the bulb evacuated, the pressure sank in a few hours as low as 0·025 microbar.

On attaching the diffusion pump to the camera the improvement was not very great, 0·04 microbar with the discharge running, but when instead it was attached to the slit system its superiority over the cooled charcoal was very pronounced. The camera pressure dropped rapidly to 0·02 microbar and on one occasion to 0·008 microbar. These tests show that the pressure in the camera is determined not so much by the vapour pressure from its surface as by the diffusion leak through the slit system, and that, when a diffusion pump is fitted to the latter, cooled charcoal is sufficient for the camera itself.

These unusually low pressures in the camera enabled a visible effect on the screen to be obtained from hydrogen rays of less than 10 kilovolts energy, much below that previously detected. The improved technique, combined with the increased sensitivity of the Q plates, enabled the method of accelerated anode rays to be applied to the new mass-spectrograph with results which will now be described.

Experiments with Cæsium.

The first mass-spectrum of cæsium was obtained by means of an anode consisting of a mixture of rubidium and cæsium chlorides on an electrically heated platinum strip.* One line only was obtained. Comparison with the rubidium lines indicated that this corresponded with a mass number 133 but, as was then pointed out, the accuracy of measurement was quite inadequate to show whether its divergence from a whole number was as large as the chemical atomic weight 132·81 suggested.

Recently K. T. Bainbridge,† working with a Dempster magnetic spectrograph of high resolving power, has confirmed the simplicity of cæsium to such a degree as to make him confident that no other isotope exists to the extent of 0·3 per cent. As he points out, on this view the atomic weight of 132·81 would imply a packing fraction of —14·3. Such a figure would be so completely abnormal that it was important to examine the matter by a method of assured reliability.

The obvious method was to photograph the line between the xenon lines 132 and 134 whose masses are known with sufficient certainty. For this purpose an anode containing CsCl with some LiBr and LiI was arranged as already described in the middle of the bulb and, after some trials, this gave a suitable cæsium line at 133. A little xenon diluted with CO_2 was then admitted, and after a few attempts the three lines 132, 133, 134 were obtained of the desired intensity. Measurements showed at once that there was no abnormality. The packing fraction of Cs 133 is barely distinguishable from that of Xe (—5·3). Its most probable value is $-5\cdot0 \pm 2$. Adopting this value and correcting for change of scale, we get

$$\text{Atomic weight of cæsium} = 132\cdot917 \pm 0\cdot02,$$

which suggests that the value 132·81 now in use is definitely too low.

Experiments with Strontium.

The improved conditions of vacuum enabled a more searching analysis of this element to be made by the method of accelerated anode rays. Using an anode containing a mixture of SrI_2 and LiBr, the strong component 88 and weak companion 86 were confirmed and in addition a third isotope 87 was discovered. The relative abundances could only be roughly estimated from the photometer readings and are as follows :—

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* 'Phil. Mag.,' vol. 42, p. 436 (1921).

† 'Phys. Rev.,' vol. 36, p. 1668 (1930).

Mass numbers of isotopes	86	87	88
Relative abundance $Sr^{88} = 100$	12	8	100
Percentage abundance	10·0	6·6	83·3

giving an isotopic moment of 0·22. The packing fraction of strontium has not been measured, but is unlikely to be very different from that of Kr^{86} which is —8·2. Assuming this and correcting for change of scale, we get

$$\text{Atomic weight of strontium} = 87\cdot 64 \pm 0\cdot 06,$$

in excellent agreement with the chemical value 87·63.

Experiments with Lithium.

The method of accelerated anode rays is not in general suited to photometry by intermittent exposures, but the improved vacuum enabling the use of low energy rays and very small discharge currents made it just feasible in the very favourable case of the alkali metals. Lithium is the easiest of all elements to handle by anode rays. Using a composite anode of graphite containing LiBr and LiI, and keeping the current at about 0·3 milliampere, it was possible to get a reasonably steady stream of 24 kilovolt rays for periods ample for the method of intermittent exposures. The contact maker was set at 8 : 1 and the most probable ratio of the peak values of the lines given by Li 7 and Li 6 was found to be 8·4. The correction for position is very large and consequently uncertain; this brings the figure to 10·2.

This must be regarded as a maximum, for, although the energies of the atoms are the same, the velocity of Li 6 is some 8 per cent. greater than that of Li 7, giving greater penetrating power which must enhance its photographic effect by a considerable but unknown amount. If we make the rough assumption that the effect is proportional to the velocity, we arrive at the round figure 11 as the most probable value for the ratio. Correcting this for packing fraction and change of scale, we get

$$\text{Atomic weight of lithium} = 6\cdot 928 \pm 0\cdot 008.$$

Many experiments have been made to determine the lithium ratio. The first made by Dempster,* using his magnetic spectrograph, gave results indicating ratios so high as 37 and so low as 4·8 with means around 7–10, and are of little value. Morand,* using a heated anode and measuring simultaneously the currents carried by Li 6 and Li 7, arrived at the figure 14·9, a ratio agreeing well with the chemical atomic weight 6·94 on the assumption that the atoms had exact whole number masses. The reliability of this result is, however, considerably reduced by the fact that Morand's apparatus was not capable of resolving the two atomic streams completely, so that the final figure was only obtained by indirect calculation.

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* 'Phys. Rev.,' vol. 18, p. 415 (1921).

Costa's measurements (1925), recalculated† with later data, indicate the masses to be 6·012 and 7·012 respectively. These combine with the chemical atomic weight to give the ratio as 12·9.

The most recent direct measurement is that of K. T. Bainbridge.‡ Using a Dempster magnetic spectrograph of high resolving power, he gives three values for the ratio 10·75, 11·28 and 11·51, and regards that of 11·28 as the most reliable.

It will be seen that the latest direct physical measurements are in good agreement with each other, and not seriously discordant with the indirect calculation from the atomic weight. It does not seem possible to accept the extremely low ratio 7·2 calculated from observations on band spectra.§

Experiments with Rubidium.

A graphite anode containing the bromide enabled rubidium to be treated in the same way as lithium, though naturally longer exposures were necessary. After correcting for position the most probable ratio of Rb 85 to Rb 87 was found to be 3·0. The packing fraction of rubidium has not been measured, but is not likely to differ much from that of Kr 86 which is —8·2. Assuming this value and correcting for change of scale, we get

$$\text{Atomic weight of rubidium} = 85{\cdot}43 \pm 0{\cdot}03,$$

in excellent agreement with the latest international value 85·44.

Experiments with Barium.

There is no reason to doubt the substantial accuracy of the chemical atomic weight of barium 137·36, but in the early mass spectra obtained from it only one line, of mass number 138, could be distinguished with certainty, hence a re-investigation with higher resolving power was desirable. The production of sufficiently intense rays from barium salts is a matter of great difficulty, but after many attempts an anode containing the chloride mixed with a little iodide yielded mass-spectra showing beyond any doubt the presence of three new isotopes, 135, 136, 137. On one spectrum only, taken with an hour's exposure, were these sufficiently intense for an approximate estimate of their relative abundances to be obtained photometrically. The fact that all these are small and in ascending order of intensity supplies a very satisfactory explanation for the failure to observe them before.* The instrument then in use was incapable of resolving them, and under these conditions they were indistinguishable from the penumbra of the much more intense line 138.

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* " Thesis for Ph.D., Paris " (1927).

† 'Proc. Roy. Soc.,' A, vol. 115, p. 509 (1927).

‡ 'Jour. Franklin Inst.,' vol. 212, p. 317 (1931).

§ v. Wijk and v. Koeveringe, 'Proc. Roy. Soc.,' A, vol. 132, p. 98 (1931); Nakamura, 'Nature,' vol. 128, p. 759 (1931).

Packing Fraction of Barium 138.—This was determined with the same arrangement of discharge as described above for cæsium. The anode contained $BaCl_2$ and LiI and the comparison line used was that at 139 due to IC, which with ICH and ICH_2 appeared strongly under these conditions. Measurements gave the packing fraction of Ba 138 to be $-6\cdot1 \pm 2$.

Barium Results.

Mass numbers of isotopes	135	136	137	138
Relative abundance $Ba^{138}=100$ ..	8	12	15	100
Percentage abundance	5·9	8·9	11·1	74·2

These figures correspond to an isotopic moment of 0·34 and give

$$\text{Atomic weight of barium} = 137\cdot43 \pm 0\cdot08,$$

in reasonable agreement with the present chemical value 137·36.

Experiments with Scandium.

The early experiments with this element† showed only one line at 45, but as it was very faint this did not disprove the presence of isotopes suggested by the chemical atomic weight 45·1. Under the more favourable experimental conditions it has been possible to repeat these experiments with an anode consisting of scandium fluoride, from the same sample as that originally used, and a little potassium bromide. The scandium line was obtained at once and by exposing for over 1 hour the intensity of this was increased to such a value that any other isotope present to the extent of 3 per cent. could have been detected. None was, which proves that scandium is simple to that degree.

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* 'Phil. Mag.,' vol. 49, p. 1193 (1925).

† 'Phil. Mag.,' vol. 47, p. 396 (1924).

The packing fraction of Sc 45 has not been determined accurately, but from its position on the plate relative to K 41 it is certain that these two are integral with each other to 1 in 2000. The chance that both these atoms have entirely abnormal masses need hardly be considered, hence a mass of 45·1 for scandium is inadmissible. From the curve the most probable packing fraction for Sc 45 is —7, and, if we assume this and correct for change of scale, we get

$$\text{Atomic weight of scandium} = 44 \cdot 96 \pm 0 \cdot 05,$$

which suggests that the chemical value 45·1 needs revision.

Experiments with Thallium.

The receipt of a sample of a volatile compound of thallium specially prepared for the purpose by Dr. v. Grosse, in collaboration with Dr. Max Bergmann, made an investigation of this element possible. Thallium ethyl, in distinction to other metal alkyls, is golden yellow in colour, and as it is unstable the anode ray experiments were interrupted so that it could be tried in the ordinary discharge without delay. Its boiling point is 64° C. at 3·0 mm., but a quantity of vapour came off even over ice showing that decomposition had already taken place. After several days' work, during which a number of plates were exposed without any result of value, the vapour pressure fell steadily and finally the thallium lines appeared.

The constitution of thallium is exactly as expected, its mass numbers are 203 and 205, the heavier predominating as in the case of rhenium. The presence of the lines of mercury in suitable strength made the determination of the relative abundance and the packing fraction unusually easy. The ratio works out to be 2·40 and the packing fraction roughly 1·8 ± 2, which, after the necessary corrections, gives

$$\text{Atomic weight of thallium} = 204 \cdot 41 \pm 0 \cdot 03,$$

in excellent agreement with Honigschmid's value 204·39 now in use, and supporting this rather than the more recent figure 204·34 given by Briscoe, Kikuchi and Peel.*

Amended Table of Isotopes.

Element.	Atomic number.	Atomic weight.	Minimum number of isotopes.	Mass numbers of isotopes in order of abundance.
Sr	38	87·63	3	88, 86, 87
Ba	56	137·36	4	138, 137, 136, 135
Tl	81	204·39	2	205, 203

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* 'Proc. Roy. Soc.,' A, vol. 133, p. 440 (1931).

Summary.

Measurements of the relative abundance of isotopes by means of the photometric of their mass-spectra have been extended to six more elements. Improvements in technique and new application of anode rays are described.

The results for the ratio of Li 7 to Li 6 support the values obtained by other direct physical methods as against those calculated from observations on band spectra.

New isotopes have been discovered in strontium and barium and the constitution of thallium determined.

Scandium is shown to be simple.

The packing fractions of cæsium, barium and thallium have been measured.

The calculated atomic weights are in good agreement with the accepted chemical values with the exception of those of cæsium and scandium.

The Slow Combustion of Methane.

By William A. Bone, D.Sc., F.R.S., and R. E. Allum, B.Sc., A.R.C.S., D.I.C.

(Received September 15, 1931.)

The slow combustion of methane was studied nearly thirty years ago by W. A. Bone and R. V. Wheeler, who showed* (i) that $2CH_4 + O_2$ mixtures react at temperatures between 300 and 400° C. and pressures of 2 to 2·3 atmospheres in borosilicate glass tubes with enormously greater velocities than do $2H_2 + O_2$ or moist $2CO + O_2$ mixtures under similar conditions, and yield CO_2, CO and H_2O without any liberation of either carbon or hydrogen, and (ii) that when $CH_4 + O_2$ mixtures were continuously circulated at between 600 and 350 mm. pressure in a closed system comprising a "reaction tube" packed with fragments of porous porcelain and maintained at temperatures between 450° and 500° C., large quantities of formaldehyde (equivalent to between 13 and 20 per cent. of the methane burnt) could be isolated from the products.

Such results, together with others on the slow combustion of ethane, ethylene and acetylene, led to the process being formulated as essentially one of successive stages of hydroxylation, thus :—

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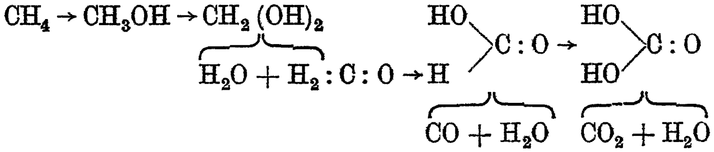
* 'J. Chem. Soc.,' vol. 81, pp. 535–549 (1902), and vol. 83, pp. 1074–1087 (1903).



$$CH_4 \rightarrow CH_3OH \rightarrow \underbrace{CH_2(OH)_2}_{H_2O + H_2:C:O} \rightarrow \underbrace{\begin{matrix}HO\\H\end{matrix}\!\!>C:O}_{CO + H_2O} \rightarrow \underbrace{\begin{matrix}HO\\HO\end{matrix}\!\!>C:O}_{CO_2 + H_2O}$$

The mechanism of hydrocarbon combustion was further discussed about a year ago in a paper on the " Slow Combustion of Ethane," by W. A. Bone and S. G. Hill,* with special reference to suggestions put forward in recent years that the *initial* stage is one of peroxidation rather than of hydroxylation; and it was proved (*inter alia*) that, at 300° C. and atmospheric pressure (i) after well-marked induction periods, $2C_2H_6 + O_2$ are much more reactive than $C_2H_6 + O_2$ mixtures, (ii) the initial product is either C_2H_6O or some less oxygenated ethane, but not $C_2H_6O_2$, (iii) its further oxidation proceeds, consistently with the hydroxylation view, *via* the successive intermediate formations of acetaldehyde, formaldehyde, formic acid and carbonic acid, to the ultimate production of steam and oxides of carbon, without any liberation of either carbon or hydrogen, although (iv) inconsiderable amounts of a " peroxide " are, or may be, formed as a concomitant of the acetaldehyde, but not earlier.

About the same time also, in a paper on the " Kinetics of Gaseous Oxidation Reactions," R. Fort and C. N. Hinshelwood described experiments on the slow oxidations of methane, methyl alcohol and formaldehyde,† which had shown in each case (i) an initial "induction period," most pronounced with methane, (ii) a dependence of the rate of reaction on the concentration of the combustible gas, and the relatively small influence of oxygen concentration, and (iii) a marked decrease in the rate of reaction in vessels of small dimensions. It was considered by the authors in question that probably " chain reactions " are much more easily propagated when the intermediate active molecules encounter more hydrocarbon than oxygen, and that " some intermediate peroxidised substance (which was neither specified nor apparently even detected) is responsible for the propagation of the chains," although it was conceded (p. 287) that the hydroxylation scheme " undoubtedly expresses the general behaviour correctly."

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* 'Proc. Roy. Soc.,' A, vol. 129, pp. 434–487 (1930).

† 'Proc. Roy. Soc.,' A, vol. 129, p. 284 (1930).

The only satisfactory evidence as to the *initial* oxidation product (whether alcohol or peroxide) would be either its unimpeachable isolation and detection, or (failing that) at least such a combination of simultaneous pressure and analytical data as would enable its nature being deduced from complete carbon-hydrogen-oxygen balances. And, in the case of ethane, such balances pointed unmistakably to the initial stage being one of "hydroxylation" rather than "peroxidation." The point is of such importance to the general theory of hydrocarbon combustion, that it was decided to re-investigate the case of methane which, as the simplest of all, would be freest from complications and most likely to afford decisive evidence. Accordingly it was arranged that while Dr. D. M. Newitt and Mr. A. E. Haffner were investigating the slow oxidation of methane at high pressures, we would study the process at atmospheric pressure and some suitable temperature range (423–447°) in such a manner as would enable us to determine (i) which is the most reactive methane-oxygen mixture, (ii) what influence (if any) have small amounts of moisture, methyl alcohol, etc., upon its "induction" and "reaction" periods, respectively, (iii) the influence of both temperature and pressure, respectively, thereon, (iv) whether or not any signs of "peroxidation" are manifested, and (v) complete carbon-hydrogen-oxygen balances throughout the whole reaction period. The principal results of our investigation, which should be read in conjunction with those recorded by Dr. Newitt and Mr. Haffner in the next paper of this issue, are embodied herein.

EXPERIMENTAL.

I.—*General Arrangements.*

Apparatus and Method.—The experimental mixtures—$3CH_4 + O_2$, $2CH_4 + O_2$, $CH_4 + O_2$, and $CH_4 + 1 \cdot 86\ O_2$—having been made up at room temperature (*circa* 18° C.) over mercury from their highly purified constituents, and then analysed,* each of them was separately introduced into the vacuous reaction vessel A (fig. 1)—a cylindrical bulb (27·5 cm. long, 5 cm. internal diameter and 586 c.c. capacity) of transparent silica—which previously had been heated up to the desired constant experimental temperature (usually 447° C.) in the electric resistance furnace B. The vessel had suitable external connection with (i) the manometer, C, (ii) a "hyvac" pump, and (iii) the gas-holder containing the experimental mixture. For further details the previous paper on the "Slow Combustion of Ethane" should be consulted.* Arrangements were made whereby, as and when desired, the vessel and its contents could be suddenly cooled at any moment by plunging it into a mixture of ice and water, so as to stop the reaction and enable the chemical composition of the medium thereat being exactly ascertained.

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* The amount of adventitious nitrogen present was usually well below 1 per cent.

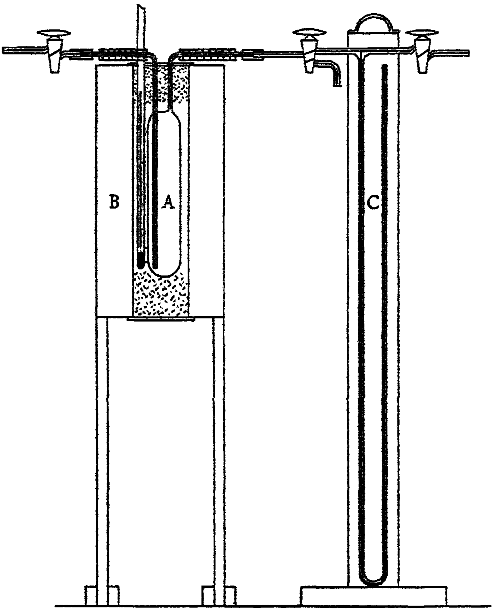

FIG. 1.—Diagram of Apparatus.

II.—*The Induction Period and General Characteristics of the Reaction.*

(*a*) As previously observed by Fort and Hinshelwood, and in keeping with former experiments in our laboratories with ethane-oxygen mixtures, the slow interaction of methane and oxygen throughout the temperature-range (423–447°) of our experiments is always homogeneous and preceded by a well-marked "induction period" during which little or no perceptible pressure or other change occurs in the system. *Certainly no sign whatever of any "peroxidation" could be detected, either during the "induction period" or at any subsequent stage of the oxidation, although the most delicate means for its detection were employed.* And in conformity with this, the $2CH_4 + O_2$ (*not* the $CH_4 + O_2$) was found to be by far the most reactive of all methane-oxygen mixtures.

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* *Loc. cit.*, pp. 438–440.

(*b*) The subsequent "reaction period" is marked by a steady pressure-rise in the system (condensation of steam being prevented) continuing until reaction has ceased, and by the production of steam and oxides of carbon, but neither free hydrogen nor carbon. The intermediate formation of formaldehyde could always be detected.

(*c*) Although both the "induction" and "reaction" periods for a given mixture at a given temperature were considerably retarded by packing the reaction vessel with fragments of silica, both were accelerated by introducing a small percentage of water vapour into the dry system; while at 447° the "induction period" was entirely obliterated, and the reaction speeded up, by the introduction of 2 per cent. of either methyl alcohol, formaldehyde, iodine or nitrogen peroxide vapour.

III.—*Comparison of Reactivities of various Moist Methane-Oxygen Mixtures at 447° C. and* 760 *to* 770 *mm.*

On making careful comparative observations upon the duration of the "induction" and "reaction" periods, respectively, when various methane-oxygen mixtures (saturated with moisture at 20° C.) were introduced into the reaction vessel at 447° C. and pressure between 760 and 770 mm., the following highly significant results, which are also set forth graphically in fig. 2 were obtained:—

Original mixture.	Durations of observed periods of		Percentage of initial oxygen remaining at end of observed reaction period.
	"Induction."	"Reaction."	
	minutes	minutes	
$3CH_4 + O_2$	10	113	4·8
	10	153	Nil
$2CH_4 + O_2$	4	36	Nil
	3	35	Nil
$CH_4 + O_2$	8	153*	29·2
	8	165*	22·5
	8	187*	24·1
	10	470	2·6
	12	1507	2·3
$CH_4 + 1·86\ O_2$	21	364*	53·1
	16	311*	53·1

* It will be seen that in these cases the oxidation had by no means finished when the experiment was broken off.

It is thus apparent that, judged whether by its " induction " or " reaction " period, the $2CH_4 + O_2$ was by far the most reactive of all the mixtures tried, requiring no more than 30 minutes for the complete disappearance of oxygen after reaction had begun. In the corresponding $3CH_4 + O_2$ and $CH_4 + O_2$ experiments the " induction periods " were always two to three times, and the " reaction periods " four or five times, longer, respectively, than with $2CH_4 + O_2$. Indeed, the " retarding " influence of oxygen over and above the last-named properties is a very remarkable feature of our results.

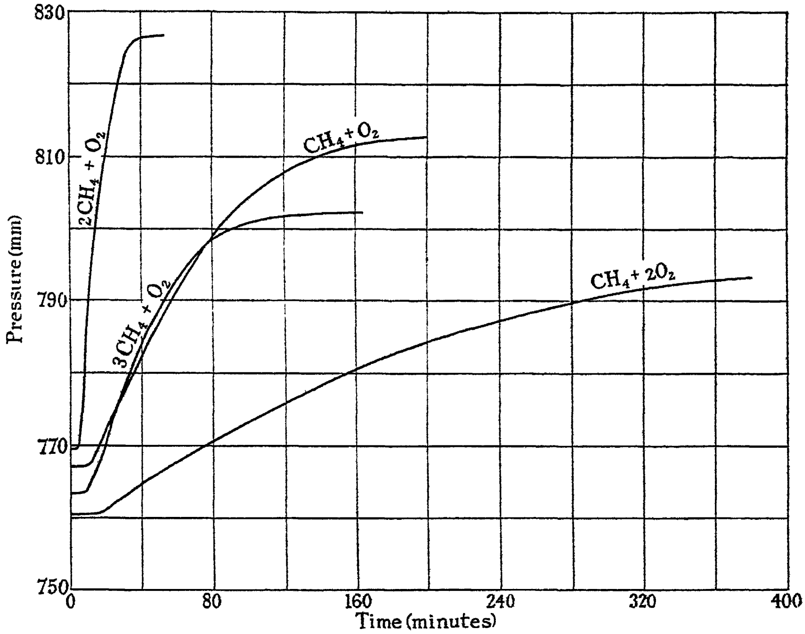


FIG. 2.—Curves showing Influence of Mixture-Composition on Rate of Reaction at 447° C. (moist).

While such facts are just what would be predicted by the " hydroxylation " theory, they seem inconsistent with that of an initial " peroxidation," which presumably would require the equimolecular (and *not* the $2CH_4 + O_2$) to be the most reactive of all methane-oxygen mixtures. And, together with Dr. Newitt's and Mr. Haffner's recent isolation of methyl alcohol as the primary product of the direct pressure-oxidation of methane (*q.v.*), they constitute as strong a proof of a primary hydroxylation as could well be desired.

IV.—*Further Experiments with the* $2CH_4 + O_2$ *Mixtures.*

Our remaining experiments with the most reactive $2CH_4 + O_2$ mixture will be briefly described with the aid of a series of pressure-time curves, and some analytical data.

(*a*) *Showing the Influences of Temperature and Pressure, respectively, upon the Induction and Reaction Periods.*—The results set forth diagrammatically in figs. 3 and 4, as well as in the following tabulated data, show how potent are both temperature and pressure in shortening the "induction" and "reaction" periods.

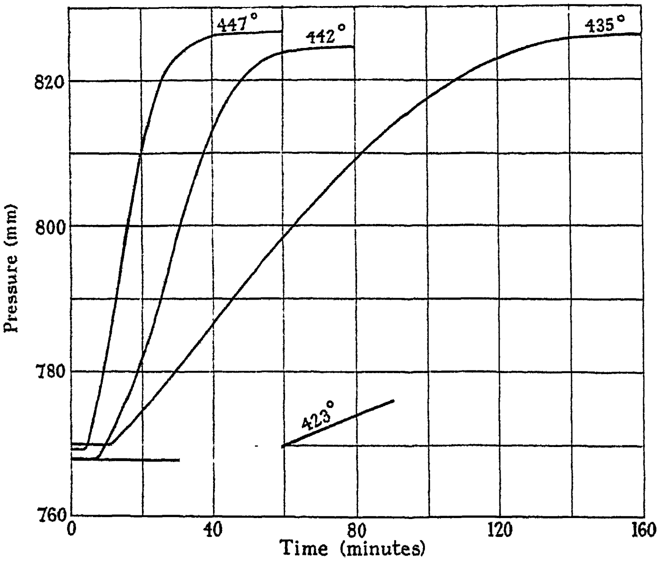


FIG. 3.—Curves showing effect of Temperature on Rate of Reaction of moist $2CH_4 + O_2$ at Normal Pressure.

(i) Influence of Temperature at Atmospheric Pressure (768–770 mm.).

Temperature.	Observed durations of	
	"Induction."	"Reaction."
° C.	minutes	minutes
447	4	36 } Reaction 98 per cent. or more complete.
442	5	65 }
435	11	150 }
423	50	—

(ii) Influence of Pressure at 447° C.

Pressure.	Observed durations of " Induction."	 " Reaction."	
mm.	minutes	minutes	
770	4	36	Reaction 98 per cent. or more complete.
706	10	160	
575	12	270	

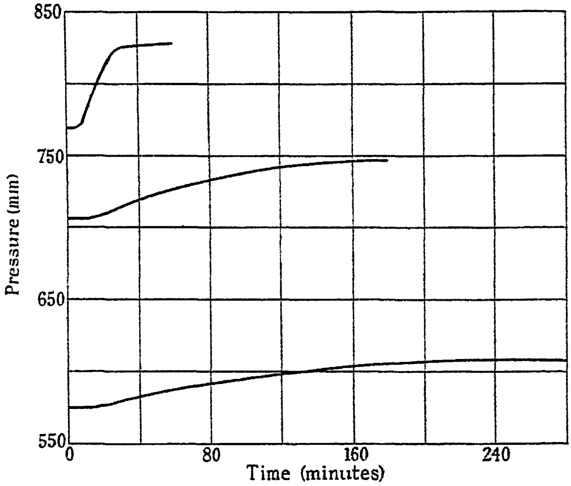


FIG. 4.—Curves showing Influence of Pressure on Moist $2CH_4 + O_2$ Mixture at 447° C.

(*b*) *Showing the Influences of Moisture and other Foreign Vapours upon the Duration of Induction and Reaction Periods, respectively, at 447° C. and Atmospheric Pressure.*—At the outset of each experiment the reaction vessel was thoroughly dried out by prolonged evacuation at 447° C.; the experimental $2CH_4 + O_2$ mixture, after being well dried by slow passage through a metre-long column of pure redistilled phosphoric anhydride, was then admitted into it at atmospheric pressure *either* in such condition (*i.e.*, in a "dry" control-experiment) or with the addition of 2 per cent. by volume of either moisture, methyl alcohol, or some other vapour. Observations of the subsequent "induction" and "reaction" periods were then taken, with results as shown graphically in fig. 5 and by the following data :—

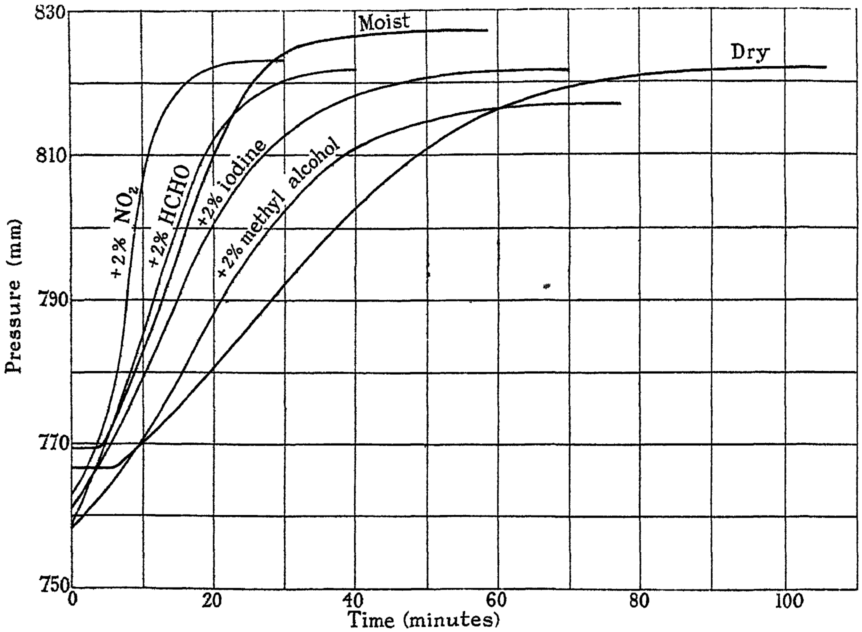


FIG. 5.—Curves showing Influence of Third Bodies on Rate of Reaction of Dry $2CH_4 + O_2$ at 447° C.

$2CH_4 + O_2$ mixture.	Total durations of	
	" Induction."	" Reaction."
Plus—	minutes	minutes
Nil, dry	6 to 7	91 to 98
2 per cent. H_2O	3 to 4	35 to 36
" CH_3OH	0	60
" $H_2:C:O$	0	40
" NO_2	0	30
" Iodine vapour	0	40

From these results it will be seen that (i) the addition of 2 per cent. of moisture to the well-dried mixture materially shortened both its " induction " and " reaction " periods at this temperature, and (ii) similar additions of other foreign vapours completely obliterated the " induction " and shortened the " reaction " period. It is interesting to note that, whereas methyl alcohol, like formaldehyde, caused the " induction period " to vanish, it quickened the " reaction period " much less than did the aldehyde.

(c) *Analytical Data showing Full Course of the* $2CH_4 + O_2$ *Interaction at* 447° *and Atmospheric Pressure.*—A complete series of experiments was made in each of which a P_2O_5-dried $2CH_4 + O_2$ mixture was introduced at atmospheric pressure into the reaction vessel at 447°. At the end of predetermined time intervals—varying from 6 minutes (*i.e.*, the end of the "induction period") to 97 minutes (or nearly the end of the "reaction period")—thereafter the vessel and its contents were suddenly plunged into a mixture of ice and water whereby reaction was stopped. Such procedure, supplemented by appropriate pressure readings, gas analyses, and tests for formaldehyde, and other possible intermediate bodies, enabled complete series of carbon-hydrogen-oxygen balances being drawn up for the system at each predetermined point during the experiment.

The full data for the whole series are given in Table I, from which the pressure-time curves shown in fig. 6 have been deduced.

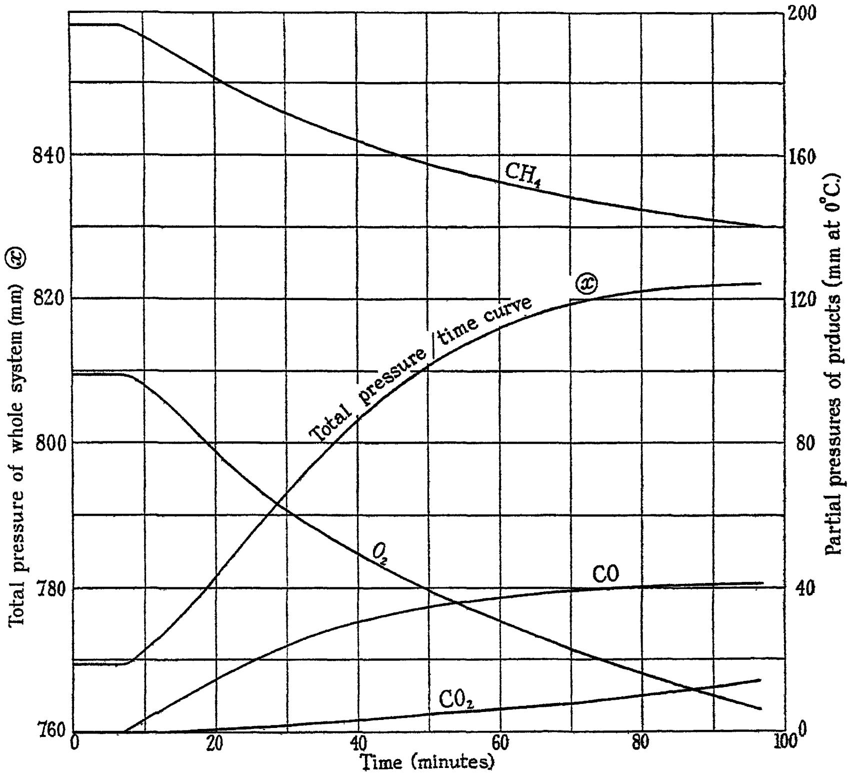


FIG. 6.—Dry $2CH_4 + O_2$ Mixture at 446·8° C.

During the "induction period" (6 minutes) no trace whatever of any "peroxide" could be detected in the system, which at the end thereof contained only methane and oxygen *plus* about 0·17 per cent. of formaldehyde

Table I.—Experiments with Dry $2CH_4 + O_2$ Mixture at T = 447° C.

	(i)			(ii)			(iii)			(iv)			(v)			(vi)		
Time in minutes from start (induction period = 6 mins.)	6			21			28			44			57			97		
	mm.			mm.			mm.			mm.			mm.			mm.		
Initial pressure of dry mixture at T° C.	761·4			769·6			758·1			760·5			759·6			762·2		
Final pressure of product (including H_2O) at T° C.	761·4			779·6			775·4			793·1			799·4			822·3		
Partial pressure of original mixture at 0° C.—	mm.			mm.			mm.			mm.			mm.			mm.		
CH_4	196·5			199·5			197·0			197·5			197·4			196·8		
O_2	97·9			99·2			98·0			98·3			98·2			98·0		
Partial pressure of gaseous products (mm.) at 0° C.—	mm.			mm.			mm.			mm.			mm.			mm.		
CO_2	Nil			0·6			1·6			3·7			5·2			14·4		
CO	Nil			18·1			17·7			32·7			35·8			40·6		
CH_4	196·0			179·0			176·7			161·0			155·8			141·3		
O_2	97·5			71·7			66·5			43·0			35·8			4·6		
Ratio O_2/CH_4 used up	—			1·34			1·53			1·52			1·51			1·68		
	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.	C.	H_2.	O_2.
C . H_2 . O_2 Balances—																		
Units in original mixture	196·5	393·0	97·9	199·5	399	99·2	197·0	394·0	98·0	197·5	395	98·3	197·4	394·3	98·2	196·8	393·6	98·0
Units in above products	196·0	392·0	97·5	197·7	358	81·3	196	353·4	77·0	197·4	322	63	196·8	311·6	58·9	196·3	282·6	39·3
Difference as H_2O (and traces of CH_2O)	0·5	1·0	0·4	1·8	41	17·9	1·0	40·6	21·0	0·1	73	35·3	0·6	82·7	39·3	0·5	111·0	58·7

vapour and a similar amount of steam (*i.e.*, $CH_2O + H_2O$) without any oxides of carbon.

As the oxidation proceeded, however, oxides of carbon *plus* further steam rapidly appeared, without much (if any) further accumulation of formaldehyde vapour in the system; the ratio of the O_2/CH_4 disappearing kept between 1·34 and 1·68 (and nearly constant at 1·5 during the middle part of the process), the ratio of the CO/CO_2 formed always keeping high and nearly constant at 10·0 during the middle part of the process. Neither carbon nor hydrogen were ever liberated; and the volumetric formation of steam always equalled that of the formaldehyde *plus* twice the combined oxides of carbon.

Moreover, analyses of the time-pressure curves reproduced in fig. 6 reveal that whereas the relative rate of CH_4-disappearance decreased, that of the O_2-disappearance increased as time progressed, a circumstance indicative of a very rapid further oxidation of intermediate products.

From first to last no trace of any "peroxide" could ever be detected, all the carbon of the methane oxidised (save the small amount always present as formaldehyde) being accounted for as $CO + CO_2$ in the gaseous products. Finally, the ratio of the H_2/O_2 unaccounted for in the cold dry gaseous products was always nearly that required for H_2O plus the small proportion of CH_2O referred to.

Considered from the hydroxylation point of view, the results showed a non-stop oxidation-run, through the mono-hydroxy and di-hydroxy stages, to steam and formaldehyde, the latter being very rapidly further oxidised to formic acid, most (about nine-tenths) of which was instantly resolved into $CO + H_2O$, the remainder being further oxidised through carbonic acid to $CO_2 + H_2O$, neither carbon nor hydrogen being liberated. The end of the "induction period" apparently synchronised with a certain very small accumulation in the system of formaldehyde, which remained fairly constant throughout the subsequent "reaction period."

V.—*Experiments with* $CH_4 + O_2$ *and* $CH_4 + 2O_2$ *Mixtures at* 448° *C.*

To complete the story, particulars are appended (Table II) of typical experiments at 448° and atmospheric pressure with $CH_4 + O_2$ and $CH_4 + 2O_2$ mixtures, respectively, These reacted so slowly, however, as to prevent our following the oxidation to completion; indeed, their chief interest lies in the evidence thus afforded of the very remarkable retardation of the whole process by oxygen. In each case the end products contained small amounts of

Table II.—Typical Experiments with $CH_4 + O_2$ and $CH_4 + 1\cdot86\ O_2$ Mixture at 448° C.

Original mixture.	Duration of		Initial pressure at 448° C.	Final pressure (including H_2O) at 448° C.	Percentage composition of cold dry N_2-free end products.				Ratio O_2/CH_4 used up.	Ratio CO/CO_2 formed.	Percentage of original O_2 used up.
	Induction period.	Observed reaction.			CO_2.	CO.	CH_4.	O_2.			
	mins.	mins.	mm.	mm.							
$CH_4 + O_2$	8	187	768·6	811·9	13·5	22·0	45·3	19·2	1·70	1·63	75·9
$CH_4 + 1\cdot86\ O_2$	16	311	761·2	793·1	9·9	15·9	23·6	50·6	1·69	1·60	47·0

formaldehyde. The ratio of the O_2/CH_4 used up was practically the same (1·7), and of the CO/CO_2 formed (1·6) was almost the same in each case.

Summary.

The results as a whole, together with those recently obtained by Dr. Newitt and Mr. Haffner for the pressure-oxidation of methane (*loc. cit.*), have demonstrated a case of direct hydrocarbon oxidation, entirely uncomplicated by any sign of "peroxidation," in which (i) the most reactive mixture is that corresponding with the alcohol-forming proportion, (ii) substantial quantities of the alcohol have actually been isolated in circumstances (chiefly high pressure) favouring its stability and survival, and (iii) all other happenings fulfilled the predictions of the hydroxylation theory.

In conclusion, we desire to thank the firm of Radiation, Ltd., of London, for their Research Fellowship, which has enabled one of us (R.E.A.) to devote his whole time to the investigation and out of which its expenses have been defrayed.

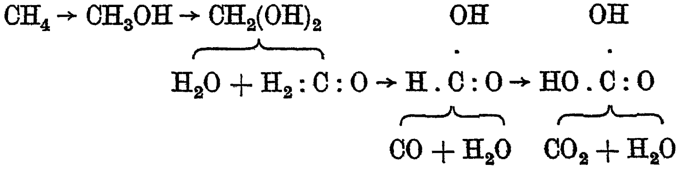
The Formation of Methyl Alcohol and Formaldehyde in the Slow Combustion of Methane at High Pressures.

By D. M. Newitt and A. E. Haffner.

(Communicated by W. A. Bone, F.R.S.—Received July 24, 1931.)

The isolation and identification of the primary oxidation product of a hydrocarbon are so important from the point of view of the theory of hydrocarbon combustion that chemists have spared no effort to overcome the difficulties involved, but so far with incomplete success.

The mechanism of the oxidation process was elucidated many years ago by the researches of Professor W. A. Bone and his collaborators as one essentially of hydroxylation, in the case of methane as involving the following stages :—



$$CH_4 \rightarrow CH_3OH \rightarrow \underbrace{CH_2(OH)_2}_{H_2O + H_2:C:O} \rightarrow \underbrace{H.\overset{OH}{\dot{C}}:O}_{CO + H_2O} \rightarrow \underbrace{HO.\overset{OH}{\dot{C}}:O}_{CO_2 + H_2O}$$

Although it is generally agreed that the main course of hydrocarbon combustion is in accordance therewith, during recent years there has been some discussion as to whether the initial product is an hydroxylated molecule or a peroxide, although the cumulative weight of experimental evidence, both direct and indirect, has been overwhelmingly in favour of the former. Thus, the initial formation of ethyl alcohol by the interaction of ethane and ozone at 100° C., the results of recent studies of the slow oxidation of methane and ethane in Professor Bone's laboratories—showing that much the fastest reacting mixtures are $2CH_4 + O_2$ and $2C_2H_6 + O_2$ and not equimolecular ones—the formation of acetaldehyde (by intermolecular change from vinyl alcohol) during the initial stages of the slow combustion of ethylene, and experiments upon the explosive combustion of methane at high initial pressures, have all pointed unmistakeably in that direction. Nevertheless, up to now, all efforts to isolate the corresponding alcohol from the products of the slow combustion of one of the simpler paraffins at ordinary pressures have been frustrated, apparently because under such conditions the further oxidation of the alcohol to the di-hydroxy stage occurs so rapidly. Hence upholders of the hydroxylation theory have always postulated an initial "non-stop" run through the mono-hydroxy to the di-hydroxy stage.

Now, however, that facilities are available at the Imperial College of Science and Technology for the systematic investigations of reactions at high pressures, it was thought desirable to study the slow oxidation of methane under such conditions. Accordingly, the experiments described herein were undertaken, with results which are decisively in favour of the hydroxylation theory, inasmuch as large proportions of methyl alcohol, but never a trace of any peroxide, have been isolated and identified from the oxidation products.

Before proceeding to describe the experiments in detail it may be well to consider the experimental conditions most likely to favour the survival of the three intermediate products. The stoichiometric and thermodynamic aspect of their formation would be as follows :—

$$(1)\quad 2CH_4 + O_2 = 2CH_3OH + \qquad 2 \times 29{,}730 \text{ cals.}$$

$$(2)\quad 2CH_3OH + O_2 = 2CH_2O + 2H_2O + \qquad 2 \times 20{,}640 \text{ cals.}$$

$$(3)\quad 2CH_2O + O_2 = 2H\,.\,COOH + \qquad 2 \times 81{,}540 \text{ cals.}$$

It will be seen that while methyl alcohol and formic acid are formed with a contraction in volume, formaldehyde involves an expansion. Hence the effect of increasing the pressure in a reacting system of methane and oxygen at a given temperature would be to favour the survival of alcohol and acid at the expense of the formaldehyde. Moreover, from free-energy considerations, an increase of temperature would accelerate all three reactions, and tend to promote the complete oxidation of the methane. A combination of high pressure with as low a temperature as possible was suggested as favouring most the survival of the alcohol.

From the kinetic standpoint, the effect of increase of pressure would be to speed up the reaction, and an additional advantage is thereby gained since it becomes possible to work at much lower temperatures than would otherwise be convenient. Precautions should be taken, however, to dissipate the heat evolved during the combustion at such a rate that no considerable rise in temperature occurs during the experiment. In the present instance this was done by diluting the theoretical methane-oxygen mixture with either a large excess of the combustible gas, or with a corresponding quantity of nitrogen carbon dioxide, or steam. The initial mixtures employed have usually had the composition $2CH_4 + O_2 + (6 \text{ to } 6\cdot5)\ X$, where $X =$ one or other of such diluents.

EXPERIMENTAL.

Apparatus and Method.

The apparatus consisted essentially of a reaction vessel heated electrically and connected (1) with cylinders containing the initial gases mixed and compressed to a suitable pressure, and (2) with an expansion chamber into which the hot products of combustion could be suddenly released at the conclusion of the oxidation or at some predetermined intermediate stage. The general arrangement of the apparatus will be clear from the diagram (fig. 1).

The reaction vessel F was constructed of nickel-chromium-molybdenum steel and was capable of withstanding a working pressure of 300 atmospheres at a temperature of 500° C.; its internal capacity was 500 c.c. The cylinder A and reserve cylinder B containing the initial gas mixture communicated through the control valve C with the inlet valve I of the reaction vessel. The expansion chamber P, having a capacity of 2 litres, was fitted with two valves K and N, the former being connected directly with the outlet valve J of the reaction vessel and the latter being used to " blow off " the wash water contained in P. The Bourdon gauge D recorded the initial pressure of the reactants at the beginning of an experiment.

The method of carrying out an experiment was briefly as follows. The reaction vessel having been brought to the desired temperature, the whole system was evacuated. About 50 c.c. of distilled water were then drawn into the expansion vessel and the valves J and K closed. By means of the control valve C the reactants were rapidly filled into the vessel F up to the desired pressure and the valve I immediately closed. During the filling process, which occupied only a few seconds, there was usually a temperature rise of about 3° due to the adiabatic compression of the gases; the temperature then fell to its original value and remained constant until the reaction started. The progress of events was followed by means of the temperature change as indicated by the readings of a platinum rhodium couple situated in a tube traversing axially the reaction chamber. When it was desired to stop the reaction, the valves J and K were opened and the contents of F rapidly expanded into the vessel P, which was then disconnected from the system. The gases and vapours remaining in the reaction vessel at a considerably reduced pressure were then passed through two cooling coils surrounded by ice and through a Jena-glass scrubber containing distilled water. Gas samples for subsequent analysis were taken at a point between the cooling coils and the scrubber, due allowance being made in the results for their alcohol content. The contents of the

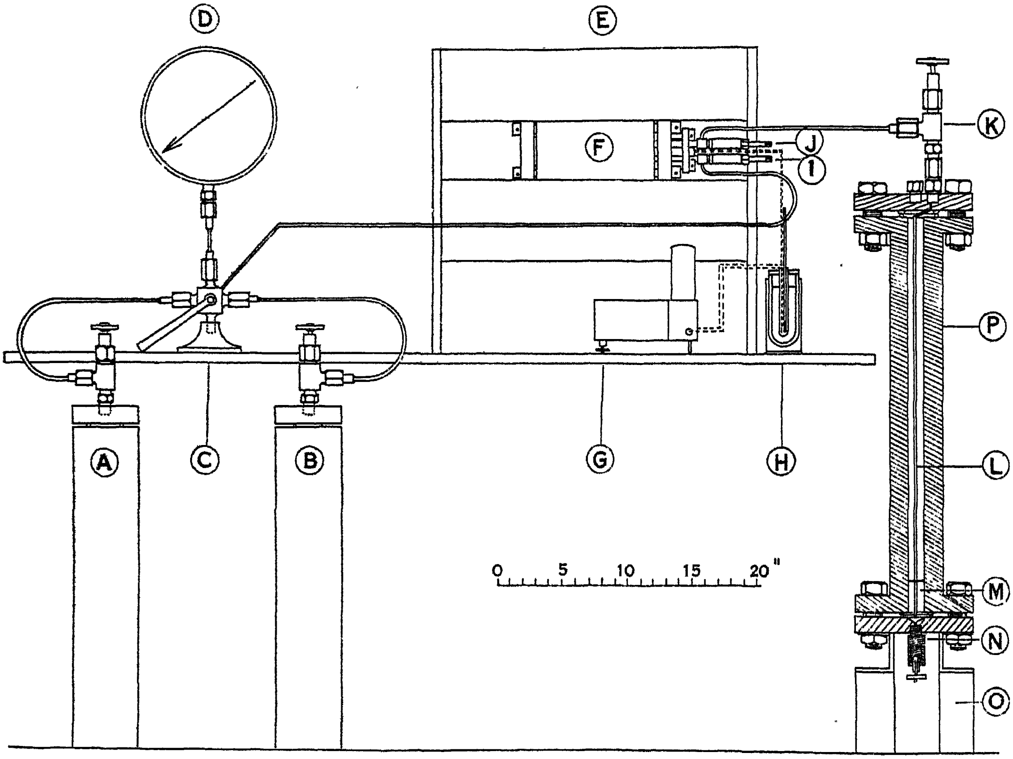


Fig. 1.

cooling coils, scrubber and expansion chamber were mixed, diluted and aliquot parts used in the estimation of methyl alcohol, formaldehyde and other products.

Preparation of Gases ; Detection and Estimation of Intermediate Oxidation Products.

Gases.—The methane used had been prepared in the Laboratory and purified both chemically and by liquefaction and fractional distillation ; after compression its purity was usually about 99·5 per cent., the remainder being nitrogen. Oxygen was purchased in cylinders from the British Oxygen Company and was used without further purification.

The methane-oxygen mixtures were made up at atmospheric pressure in a 10 cubic foot gas-holder and were compressed in cylinders to 200 atmospheres.

Methyl Alcohol.—In the early stages of the investigation the condensable products from a number of experiments were collected and used for qualitative tests. Methyl alcohol was identified by preparing therefrom (1) methyl salicylate and (2) a specimen of methyl *p*-nitrobenzoate. For the latter preparation the liquid from the cooling coils, after three successive experiments, was dried over quicklime for 12 hours and distilled below 90° C. The distillate was treated with *p*-nitrobenzoyl chloride, gently warmed and the methyl derivative precipitated by pouring into water. After repeated recrystallisation it gave a melting point of 95° C.

The quantitative estimation was carried out by the method of Fischer and Schmidt, slightly modified in detail to accelerate the reaction. The method consists essentially in converting the alcohol to methyl nitrite, hydrolysing the ester in the presence of acid potassium iodide, and estimating the iodine liberated by means of a standard sodium thiosulphate solution in the usual way.

Formaldehyde was detected by Schiff's reagent, and estimated by Romijin's potassium cyanide method. In a few cases the total aldehydes were also estimated by Ripper's bisulphite method ; but, as no appreciable difference was obtained by the two methods, higher aldehydes were assumed to be absent.

Formic Acid.—The condensate was warmed to liberated carbon dioxide and titrated with N/100 alkali. Only traces of formic acid, too small to estimate with accuracy, were found.

Peroxides were tested for by the titanic sulphate reaction ; but, although the method is sensitive to 1 part in 500,000, no trace of their presence was ever detected.

Special tests were also made with the object of detecting any (i) dimethylether, possibly formed by the dehydration of methyl alcohol, and (ii) acetals, but with entirely negative results in each case.

The General Characteristics of the Reaction at High Pressures.

As an example of the behaviour of methane-oxygen mixtures undergoing reaction at high pressures, the course of an experiment at 106·4 atmospheres pressure may be described, as being typical of all those included in the present paper. In this case the initial mixture consisted of the two gases in the proportion of 8·1 parts of methane to 1 part of oxygen, the reaction temperature being 341° C. The curves in fig. 2 show the rate of disappearance of oxygen and the rate of change of temperature from the moment of filling until the reaction was substantially complete.

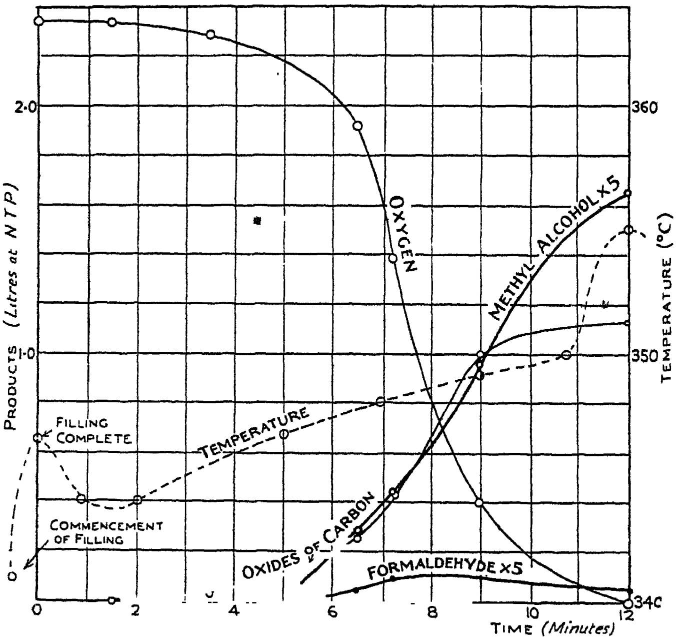


Fig. 2.

Considering first the temperature-time curve, it will be seen that an initial rise of some 3° took place due to the adiabatic compression of the gases on filling; after 3 minutes the temperature had fallen nearly to its original value, but almost immediately thereafter it commenced to rise, and between $6\frac{1}{2}$ and 8 minutes increased rapidly. At 12 minutes it had reached a maximum and was again diminishing. The oxygen-time curve indicates the existence of an induction period of some 3 minutes, during which no detectable diminution in the oxygen content of the mixture took place; this was succeeded by a period of rapid reaction during which the rate of oxygen disappearance showed a rough parallelism with the rate of temperature rise; at maximum temperature no uncombined oxygen remained. The occurrence of this induction period, similar to that found by Bone and Hill in the oxidation of ethane and by Fort and Hinshelwood for ethylene, methane, and methyl alcohol, is typical of the high pressure reaction and under certain conditions may amount to as much as 80 minutes.

Although under the foregoing conditions the reaction in a steel vessel is predominantly heterogeneous, its rate being increased several times by increasing the surface/volume ratio of the reaction vessel, indications were obtained of its becoming homogeneous at higher temperatures. Such was manifested by an unusually high temperature increase and by an abrupt fall in the amount of methyl alcohol surviving in the product (see Table II) with probable occurrence of flame in the mixture, although subsequent examination showed no carbon to have been deposited during the reaction. In this connection it may be recalled that Bone, Newitt and Smith* found that a methane-air mixture containing 41·4 per cent. of methane could be exploded at an initial pressure of 134·1 atmospheres without any liberation of carbon, although a 38·1 per cent. mixture under identical conditions gave a copious deposit.

Three series of experiments were carried out to determine (1) the quantity of alcohol present in the system at various times during the reaction, and (2) the effect of initial pressure and temperature upon the yields of alcohol obtained in the products when the free oxygen present had completely disappeared.

Detailed Study of the Initial Stages of the Oxidation.

Before proceeding to investigate the effect of pressure and temperature on the course of the combustion, experiments were carried out with a $8 \cdot 1CH_4 + O_2$ mixture with a view to ascertaining the change in the rates of formation of methyl alcohol and formaldehyde, respectively, as the relative concentration of oxygen in the reacting system progressively diminished; for, since the disappearance of oxygen is accompanied by a corresponding increase in the ratio CH_4/O_2, the conditions for the formation of the primary product would appear to become increasingly favourable as combustion proceeds.

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* "Gaseous Combustion at High Pressures" (Longmans, Green & Co.), 1929.

The method employed was to carry out a number of experiments at constant temperature and pressure and to stop the reaction after various time intervals by suddenly expanding and cooling the system in the manner already described. Two series of experiments were made commencing in each case with a $8\cdot1CH_4 + O_2$ mixture at initial pressures of 48·0 and 106·4 atmospheres respectively. The results are summarised in Table I and, in the case of the series at the higher pressure, are illustrated by means of curves in fig. 2, above.

Table I.—The Amounts of Methyl Alcohol and Formaldehyde present at various Stages during the Slow Oxidation of Methane at High Pressures.

Duration of experiment.	Composition of gaseous medium, c.c. at N.T.P.						Ratios.	
	O_2.	CH_4.	CO_2.	CO.	CH_3OH.	H.CHO	CO/CO_2.	$CH_3OH/H.CHO$.
Initial pressure = 106·4 atmospheres. Temperature = 341° C.								
minutes								
0	2332	18790	—	23	—	—	—	—
6·5	1905	18360	191	82	59	8	0·31	7·4
7·25	1390	18330	334	120	115	16	0·28	7·2
9·0	413	17570	564	460	192	17	0·77	11·3
12·0	Nil	17310	461	695	330	10	1·45	33·3
30·0	Nil	17240	766	502	325	4	0·63	81·2
1000·0	Nil	17480	1030	160	147	3	0·13	49·0
Initial pressure = 49·0 atmospheres. Temperature = 373° C.								
0	1033	8036	—	27	—	—	—	—
3	655	7846	144	59	9	3	0·22	3·0
4	565	7866	197	59	25	6	0·16	4·1
4·5	Nil	7316	645	50	109	5·5	0·03	19·8
5·5	Nil	7266	529	201	114	5	0·33	22·8

From an inspection of the figure it will be seen that, following an induction period of about 3 minutes, during which time no detectable change in the composition of the mixture took place, the oxidation commenced, at first slowly and then with increasing velocity, until after the lapse of 12 minutes the whole of the oxygen had been consumed. Both methyl alcohol and formaldehyde were detected at a very early stage and the methyl alcohol increased in concentration with time, its actual rate of formation (as derived from the concentration-time curves) showing a progressive increase as the ratio CH_4/O_2 in the system increased, until towards the end when there was a marked slowing down. Peroxides and hydrogen were tested for with negative results.

Both carbon monoxide and dioxide were found in quantities representing in all cases upwards of 70 per cent. of the methane burnt. The CO/CO_2 ratios are somewhat irregular, but in general showed an increase with time; thus, in the series at 106·4 atmospheres, the ratio after 6·5 minutes is 0·31 and after 12 minutes is 1·45 and a similar result is observed at the lower pressure.

In two experiments at 106·4 atmospheres the products were allowed to remain in the reaction vessel for 18 minutes and 16½ hours, respectively, after all the oxygen had disappeared. During this time some interaction occurred, both the amounts of alcohol and aldehyde diminishing, although they never entirely disappeared; the CO/CO_2 ratio showed a rapid fall to 0·63 in the former case and 0·13 in the latter.

The Effect of Temperature upon the Survival of Methyl Alcohol and Formaldehyde in the Products.

In the experiments of this series pressures of 150, 106·4 and 48·2 atmospheres were employed, the initial mixture having the same composition as before.

The method consisted in charging the reaction vessel, previously heated to a selected temperature, with the $8 \cdot 1CH_4 + O_2$ mixture and then following the progress of events by the temperature change. Immediately after the temperature had reached a maximum the contents of the vessel were rapidly expanded and cooled and the products treated in the manner already indicated.

The main features brought out by the experimental results, which are summarised in Table II and illustrated by means of curves in fig. 3, are as follows:—

(1) At each pressure there was a definite temperature at which maximum survivals of alcohols and aldehydes were obtained. This was by no means the lowest temperature at which oxidation would take place, but was usually one giving a medium time of reaction. For example, at 106·4 atmospheres a yield of methyl alcohol corresponding with 22·3 per cent. of the methane burnt was obtained at 341° C., at which temperature there was an induction period of 2·5 minutes followed by a reaction time of 9·5 minutes. When the induction period was extended to 53 minutes and the reaction time to 35 minutes, the yield was only 10·1 per cent., although the temperature was some 3° lower. A similar diminution was noticed when the temperature was too high and the duration of reaction correspondingly short.

Table II.—The Effect of Temperature upon the Survival of Methyl Alcohol and Formaldehyde in the Products of Methane Oxidation at High Pressures.

Initial mixture, $CH_4/O_2 = 8{\cdot}1/1$.

Initial temperature.	Rise in temperature.	Duration of—		Ratio CO/CO_2 in gaseous products.	Survival as per cent. on methane burnt.		Ratio CH_3OH/ H. CHO.
		Induction.	Reaction.		CH_3OH.	H . CHO.	
Initial pressure = 48·2 atmospheres.							
° C.	° C.	mins.	mins.				
360	7	14	12	0·28	3·2	0·5	6·4
367	7	7	8	0·04	5·2	0·5	10·4
370	9	5	4	0·15	11·2	0·7	16·0
373	12	1·5	4	0·21	13·7	0·7	19·6
375	—	—	2	0·21	13·7	0·8	17·1
377	12	1	2·5	0·08	12·5	0·9	13·9
393	16	—	1	0·21	11·0	0·7	15·7
Initial pressure = 106·4 atmospheres.							
336	4	53	35	0·05	10·1	0·30	33·6
339	10	14	22	0·01	14·1	0·36	39·2
341	14	2·5	9·5	1·5	22·3	0·75	29·4
343	10	—	12	1·0	20·0	0·93	21·5
347	17	2·5	5·5	—	16·6	0·30	55·3
352	26*	1	1	3·9	9·8	0·95	10·3
355	37*	0	1	4·2	3·8	Trace	—
Initial pressure = 150 atmospheres.							
335	13	14	33	0·04	11·9	0·3	39·6
341	17	5	11	0·06	19·0	0·6	31·6
343	32	—	instantaneous	2·1	21·1	0·4	52·7

* Probable formation of flame during combustion.

(2) The ratio of CO/CO_2 in the products remained fairly constant with temperature in the series at 48·2 atmospheres, but showed a definite increase at the remaining two pressures. In two experiments at 106·4 atmospheres pressure the ratio showed an exceptionally large value, the figures being 3·9 for 352° C. and 4·9 for 355° C.; this increase corresponded with an abrupt fall in the alcohol and aldehyde figures and probably indicated the formation of flame in the vessel; no carbon was deposited in either case nor was any hydrogen found in the products.

(3) A comparison of the ratios of alcohol/aldehyde at the various temperatures showed that whilst temperature had no definite influence, there was a marked increase as the initial pressure was raised. Thus, taking the mean of all the results at each pressure, the figures were :—

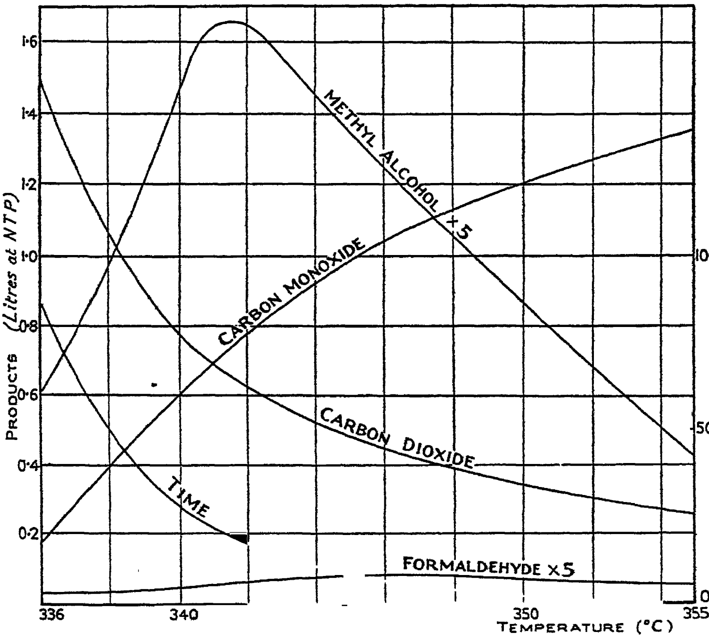

FIG. 3.

Initial pressure.		Ratio $CH_3OH/H.CHO$.
48·2	....	13·0
106·4	....	31·5
150·0	....	41·6

The Effect of Initial Pressure on the Survival of Methyl Alcohol and Formaldehyde.

A consideration of the results included in Table II showed that to obtain comparative figures for the effect of pressure it would be necessary to vary the temperature so that in every case the maximum survivals of alcohol and aldehyde were obtained ; this involved the carrying out of a large number of experiments at different temperatures and pressures on the lines of those recorded in the preceding section.

In the results, which are set forth in Table III for a $8 \cdot 1CH_4 + O_2$ mixture, the pressure range 10 to 149 atmospheres has been covered ; and, with the

Table III.—The effect of Initial Pressure upon the Survival of Methyl Alcohol and Formaldehyde in the Products at Various Temperatures. Initial mixture = $8 \cdot 1CH_4 + O_2$.

Initial pressure.	Initial temperature.	Rise of temperature.	Duration of oxidation.	Ratio CO/CO_2 in gaseous products.	Survival as per cent. on methane burnt.		Ratio $CH_3OH/H.CHO$.
					CH_3OH.	$H.CHO$.	
atms.	° C.	° C.	mins.				
10	400	2	10	0·06	1·1	Nil	—
25	385	4	7	0·15	4·8	0·66	7·3
40*	372	6	15	0·05	6·1	1·20	5·1
48	373	12	4	0·35	13·7	0·8	17·1
106·4	341	14	12	—	22·3	0·75	29·7
149*	341	17	16	0·08	19·0	0·60	31·6

* Not quite optimum temperature conditions.

possible exception of experiments at 40 and 149 atmospheres, the data may be taken as fairly representing the maximum survival under the given experimental conditions, at the pressures in question.

The figures require little comment; in general, the effect of pressure was not only to increase the survival of alcohol, and, to a lesser extent of aldehyde, but also to increase the ratio $CH_3OH/H.CHO$. It will be noticed that in all cases the best results were obtained when the time of oxidation was between 4 and 12 minutes and when the temperature rise during the experiment did not exceed 14° C.

The Effect of Diluents upon the Combustion.

Experiments were next carried out to determine the effect (1) of inert diluents, and (2) of the non-combustible products of combustion (steam and carbon dioxide) on the reaction. For this purpose mixtures of composition $2CH_4 + O_2 + 6 \cdot 5X$, where $X = CO_2$, H_2O or N_2, were employed, and in each case the reaction was allowed to proceed to completion and the products analysed. A control experiment in which the diluent was replaced by its equivalent of methane was made for purposes of comparison.

The principal results of one such series at an initial pressure of 50 atmospheres are summarised in Table IV. It will be seen from a comparison of the figures with those in Table II that no matter whether the diluent was an inert gas or one of the non-combustible products of combustion, the effect was to slow down the rate of reaction to such an extent that, in order to obtain

Table IV.—The Survival of Methyl Alcohol and Formaldehyde in the Slow Combustion of $2CH_4 + O_2$ Mixtures diluted with Nitrogen, Carbon Dioxide and Steam.

Initial pressure = 50 atmospheres.

Initial mixture $2CH_4 + O_2 +$.	Temperature.	Temperature rise.	Time of reaction.	Amount of CH_3OH and H. CHO surviving in products. c.c.'s at N.T.P.		Ratio CH_3OH/ H. CHO.
				CH_3OH.	H . CHO.	
	° C.	° C.	mins.			
6·5 N_2	397	3	16	48	2·7	17·9
6·5 H_2O	400	2	2	43	1·6	26·9
6·5 CO_2	390	4	8	50	3·0	16·7
Control experiment						
6·5 CH_4	397	12	1	80	4·6	15·7

times of reaction comparable with those for the simple $CH_4 - O_2$ mixture, it was necessary to employ temperatures nearly 20° higher. As might be expected, the higher temperatures led to a diminution in the concentrations of methyl alcohol and formaldehyde surviving in the products; but, in addition, the control experiment shows that the observed diminution in yields is not entirely a temperature effect, but arises partly from the substitution of the excess methane in the standard $8{\cdot}5CH_4 + O_2$ mixture by the diluents.

Under the conditions of our experiments methyl alcohol, carbon monoxide and hydrogen all oxidise readily and only survive in the products of combustion of methane when oxygen is in defect of that required for its complete oxidation to carbonic anhydride and steam.

Summary.

It has been shown that:—

(1) In the slow combustion of methane at high pressures considerable quantities of the primary product, methyl alcohol, survive and can be isolated.

(2) As combustion proceeds in an $8{\cdot}1CH_4 + O_2$ mixture the rate of formation of methyl alcohol increases with the CH_4/O_2 ratio until a point is reached when the concentration of steam and carbon dioxide in the products begin to exert a retarding effect.

(3) At any particular pressure there is a definite temperature at which optimum amounts of methyl alcohol and formaldehyde survive.

(4) The effect of increasing pressure is not only to increase the amounts of both products surviving, but also to increase the ratio $CH_3OH/H.CHO$.

(5) The oxidation of methane under the experimental conditions described is mainly a surface effect and is characterised by a marked induction period.

In conclusion, one of us (A.E.H.) desires to express his thanks to the Gas Light & Coke Company, whose Gas Research Fellowship has enabled him to devote his whole time to the work.

The Third Spark Spectrum of Arsenic (As IV).

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Introductory.

The third spark spectrum of Arsenic has been investigated in the extreme ultra-violet by Sawyer and Humphreys,* who have found the three triplet combinations of the deep term $4p\,^3P$ with $5s\,^3S$, $4d\,^3D$ and $4p^2\,^3P$ and the singlet resonance line $4s\,^1S_0 - 4p\,^1P_1$. Two more triplets involving the term $5p\,^3P$ were discovered later by the writer.† The present paper deals with the identification of the higher members of the triplet system as well as the singlets and inter-combination lines of the spectrum. Most of the lines which could be assigned to the trebly-ionised atom of Arsenic have been classified and it is now possible to estimate the absolute values of the characteristic terms.

Experimental.

The general experimental methods employed in the present investigation on the spectrum of Arsenic have been briefly described already in two previous communications‡ dealing with the arc and the second spark spectrum of Arsenic. For the excitation of the third spark spectrum, the chief source which has proved useful is a condensed discharge through Arsenic vapour contained in a capillary tube of about ½ or 1 mm. bore. Constant heating of the tube was found necessary, in order to have sufficient pressure of the vapour in the capillary and to maintain a steady discharge. After running the tube for a few hours, however, it was found to require very little attention. The lines of As IV are but feebly represented in a spark in hydrogen and are absent altogether in a spark in air between two poles of the metal. This has made possible the selection of the lines belonging to the fourth stage of ionisation of the atom. In the extreme ultra-violet below λ 1400, the chief source employed was a highly condensed spark *in vacuo* between aluminium electrodes containing arsenic. These photographs were taken with a Siegbahn vacuum spectrograph at Upsala; the method has been described fully elsewhere.* As in the case of selenium, a coil of self-inductance consisting of 31 turns of copper wire 0·4 mm. thick, 60 cms. long and 73 cms. in diameter, served the purpose of distinguishing the lines due to the different stages. Lines of As II and As III were present in this inductance spectrum strongly, while those of As IV were considerably weakened and those of As V absent altogether.

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* Sawyer and Humphreys: 'Phys. Rev.' vol. 32, p. 583 (1928).

† K. R. Rao: 'Nature,' Feb. 16 (1929).

‡ K. R. Rao: As I, 'Proc. Roy. Soc.' A, vol. 125, p. 238 (1929), and As III, 'Proc. Phys. Soc.' vol. 43, 68 (1931).

Of the existing measurements of the spectrum of arsenic, it may be pointed out that those by Herpertz,† which extend between λ 5903 and λ 2302, appear to have been made with a source in which the lines of singly and doubly ionised atoms frequently occur; the excitation used by Queney‡ seems, however, to have been much higher, but these measurements do not extend above λ 2495. With a few exceptions, the lines recorded by Bloch§ are due to As I.

Results.

Being similar to Zn I, Ga II and Ge III, the spectrum of As IV consists of a simple triplet and singlet system. The important terms, predicted from Hund's theory, are shown in Table I, the notation being the same as that adopted by the writer in previous papers.

The first clue to the identification of the series was the sharp triplet at λ 3109, which appeared but faintly in the spark in hydrogen and was considerably enhanced in the discharge tube. It also gave the inverted group $4d\,{}^3D - 5p\,{}^3P$ in the calculated position. A further search revealed two more triplets which confirmed the above $5p\,{}^3P$ intervals. The singlets were obtained, to

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* K. R. Rao and J. S. Badami: 'Proc. Roy. Soc.,' A, vol. 131, p. 154 (1931).

† Kayser: Handbuch, vol. 5, p. 109.

‡ Queney: 'J. Physique,' vol. 10, p. 448 (1929).

§ Bloch: 'J. Physique,' vol. 4, 622 (1914), and 'C.R.,' vol. 171, p. 709 (1920).

Table I.—Predicted Terms in As IV.

3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	Term Prefix.	Terms.
2	6	10	2							$4s$	^1S
2	6	10	1	1						$4p$	$^3P\ ^1P$
2	6	10	1				1			$5s$	$^3S\ ^1S$
2	6	10	1		1					$4d$	$^3D\ ^1D$
2	6	10	1			1				$4f$	$^3F\ ^1F$
2	6	10		2						$4p^2$	$^3P\ ^1D\ ^1S$

start with, by correlating the iso-electronic spectra Zn I to Se V. The lines λ 1480·61 and λ 1299·34 occurred in the respective extrapolated positions for $4p\,^1P_1 - 4d\,^1D_2$ and $4s\,^1S_0 - 4p\,^3P_1$, and their behaviour was in keeping with their assignment to the trebly-ionised atom. These led to the identification of further inter-combinations in the vacuum grating region. The differences 133 cm.$^{-1}$ and 206 cm.$^{-1}$ of the term $4d\,^3D$ occurred in the strong triplet at λ 1350, which could be no other than the combination $4d\,^3D - 4f\,^3F$.

In Table II are collected all the combinations of As IV, including those given by Sawyer and Humphreys. The second members of the series $4p\,^3P - ms\,^3S$

Table II.—Multiplets in As IV.

$5p$	$^3P_0$ 153157·0	*254·9*	$^3P_1$ 152902·1	*818·1*	$^3P_2$ 152084·0	*1754·9*	$^1P_1$ 150329·1
$5s\,^3S_1$ = 184241·4	31084·2 (4)	*255·3*	31339·5 (6)	*817·9*	32157·4 (8)		33912·1 (1)
$^1S_0$ = 174948·5			22049·8 (0) ?				24619·4 (6)
$4d\,^3D_1$ = 193772·0 *132·8*	40614·5 (9)	*254·8*	40869·7 (8)	*818·3*	41688·0 (2)		43443·2 (2)
$^3D_2$ = 193639·2 *202·8*			40737·0 (10)	*817·8*	41554·8 (6)		43310·6 (3)
$^3D_3$ = 193436·4					41352·0 (10)		
$^1D_2$ = 224806			71905 (0)	*818*	72724 (10)*		74477 (7)
$5d\,^3D_1$ = 108788·2 *58·2*	44369·3 (8)	*254·9*	44114·4 (5)	*818·6*	43295·8 (1)		41540·8 (2)
$^3D_2$ = 108730·0 *91·2*			44172·1 (9)	*818·1*	43354·0 (5)		41599·4 (3)
$^3D_3$ = 108638·8					43445·2 (9)		
$^1D_2$ = 110534·6			—		41549·4 (2)		39794·1 (6)
$6s\,^3S_1$ = 105493·9	47662·9 (3)	*254·5*	47408·4 (4)	*818·3*	46590·1 (5)		—
$^1S_0$ = 103670·1			—				46659·0 (4)

* Coincident with a strong line of As II.

Table II—(continued).

$4p$	$^3P_0$ 328557	*1150*	$^3P_1$ 327407	*2530*	$^3P_2$ 324877	*32530*	$^1P_1$ 292347
$4s\,^1S_0$ = 404369			76962 (10)				112022 (10)
$5s\,^3S_1$ = 184241·4	144313 (5)	*1149*	143164 (7)	*2531*	140633 (8)		108103 (1)
$^1S_0$ = 174948·5			152467 (0)				117407 (10)
$4d\,^3D_1$ = 193772·0 *132·8*	134784 (8)	*1153*	133631 (8)	*2526*	131105 (4)		—
$^3D_2$ = 193639·2 *202·8*			133767 (9)	*2532*	131235 (8)		—
$^3D_3$ = 193436·4					131441 (10)		
$^1D_2$ = 224806			102605 (9)	*2530*	100075 (9)		67540 (9)
$4p^2\,^3P_0$ = 224435 *1534*			102973 (10)				67909 (1)
$^3P_1$ = 222901 *2926*	105658 (9)	*1151*	104507 (9)	*2526*	101981 (10)		69444 (2)
$^3P_2$ = 219975			107435 (8)	*2531*	104904 (8)		72371 (6)
$^1D_2$ = 199711			—		—		92636 (7)
$^1S_0$ = 192686			—		—		99661 (8)
$5d\,^3D_1$ = 108788·2 *58·2*	[219769]		[218619]		[216089]		
$^3D_2$ = 108730·0 *91·2*			[218677]		[216147]		
$^3D_3$ = 108638·8					[216238]		
$^1D_2$ = 110534·6							181808 (1)
$6s\,^3S_1$ = 105493·9	[223063]		[221913]		[219383]		
$^1S_0$ = 103670·1							188569 (2)

Note.—The groups $4p\ ^3P - 4d\,^3D$, $4p\ ^3P - 5s\ ^3S$, $4p\ ^3P - 4p^2\ ^3P$, and $4s\ ^1S - 4p\ ^1P$ are identifications by Sawyer and Humphreys.

$4f$	$^3F_2$ 119913	*274*	$^3F_3$ 119639	*413*	$^3F_4$ 119226	*587*	$^1F_3$ 118639
$4d^3D_1$ = 193772·0 *132·8*	73859 (6)						
D_2 = 193639·2 *202·8*	73727 (2)		74001 (7)				75009 (2)
$^3D_3$ = 193436·4	[73511]		73798 (2)		74211 (9)		74806 (0)
$^1D_2$ = 224806	—		—				106167 (5)

and $4p\,{}^3\mathrm{P} - md\,{}^3\mathrm{D}$ lie lower down in the extreme ultra-violet beyond the region investigated by the writer, but as they are expected to be fairly strong their calculated positions have been included in the Tables, enclosed in brackets.

Other combinations.

$4p^2\,{}^3\mathrm{P}_2 - 5p\,{}^3\mathrm{P}_2 = 67879$ (1)
$- 5p\,{}^1\mathrm{P}_1 = 69645$ (4)
$- 4f\,{}^3\mathrm{F}_2 = 100054$ (2)
$4p\,{}^1\mathrm{P}_1 - \alpha = 186092$ (3)
$5p\,{}^1\mathrm{P}_1 - \alpha = 44076{\cdot}9$ (4) $\alpha = 106252$
$5p\,{}^1\mathrm{P}_1 - \beta = 40572{\cdot}1$ (3) $\beta = 109757$
$5p\,{}^1\mathrm{P}_1 - \gamma = 43905{\cdot}8$ (3) $\gamma = 106423$
$5p\,{}^3\mathrm{P}_2 - \beta = 42328{\cdot}0$ (2)
$5p\,{}^3\mathrm{P}_2 - \gamma = 45662{\cdot}7$ (0)

It may be worth while referring to the peculiarities in the intensities of some of the lines, particularly as they are found to be characteristic of all the spectra hitherto known which arise from the configuration of two *s* electrons. The inter-combination lines $4p\,{}^3\mathrm{P}_{1,\,2} - 4d\,{}^1\mathrm{D}_2$ are abnormally strong, being sometimes more intense than even the singlet line $4p\,{}^1\mathrm{P}_1 - 4d\,{}^1\mathrm{D}_2$. But, on the other hand, the lines $4p\,{}^1\mathrm{P}_1 - 4d\,{}^3\mathrm{D}_{1,\,2}$ are faint or altogether absent, although the term $4d\,{}^3\mathrm{D}_{1,\,2}$ combines with the higher Rydberg term $5p\,{}^1\mathrm{P}_1$ to give fairly strong lines. The exceptional intensity of the inter-combination $4p^2\,{}^3\mathrm{P}_2 - 4p\,{}^1\mathrm{P}_1$ is remarkable, while the other lines of this group, $4p^2\,{}^3\mathrm{P}_{1,\,0} - 4p\,{}^1\mathrm{P}_1$, are feeble.

The intervals of the triplet terms also exhibit interesting features. Comparing the $4d\,{}^3\mathrm{D}$ and $4f\,{}^3\mathrm{F}$ intervals in the ZnI– like spectra as in Table III, it is surprising to see that the ${}^3\mathrm{F}$ intervals in As IV are relatively large, being almost double the ${}^3\mathrm{D}$ separations.

In the case of a pure Russell-Saunders type of coupling it is to be expected that the separations $4p\,{}^3\mathrm{P}_0 - 4p\,{}^3\mathrm{P}_2$ as well as $4p^2\,{}^3\mathrm{P}_0 - 4p^2\,{}^3\mathrm{P}_2$ should be slightly smaller than $4p\,{}^2\mathrm{P}_1 - 4p\,{}^2\mathrm{P}_2$ of the next higher ion. But, as Sawyer

Table III.—${}^3\mathrm{D}$, ${}^3\mathrm{F}$ intervals in Zn I–like Spectra.

Spectrum	$4d\,{}^3\mathrm{D}_{1,\,2}$; ${}^3\mathrm{D}_{2,\,3}$	$4f\,{}^3\mathrm{F}_{2,\,3}$; ${}^3\mathrm{F}_{3,\,4}$
Zn I	3·4 ; 5·5	Unresolved
Ga II	25 ; 34	,,
Ge III	70·8 ; 106·5	17·4 ; 63·3
As IV	132·8 ; 202·8	274 ; 413

and Humphreys have pointed out, when we consider the isoelectronic sequence Zn I to Se V, there is a gradual relative increase of the $4p^2\,{}^3P$ separation with respect to the $4p\,{}^2P$ interval, and is to be ascribed to a departure from the above simple type of coupling. Such a departure is evident also when we examine, as in Table IV, the interval ratios of the $mp\,{}^3P$ terms in the spectra under consideration.

Table IV.—^3P interval ratios.

Spectrum	$\dfrac{\Delta\nu\,4p\,{}^3P_{1,2}}{\Delta\nu\,4p\,{}^3P_{0,1}}$.	$\dfrac{\Delta\nu\,5p\,{}^3P_{1,2}}{\Delta\nu\,5p\,{}^3P_{0,1}}$.
Zn I	2·05	2·10
Ga II	2·09	2·36
Ge III	2·15	2·72
As IV	2·20	3·28
Se V	2·26	—

The deviation from the normal type appears to be increasing gradually with increase of nuclear charge, as, in the case of both the ^3P terms, the ratio departs more and more from the theoretical value 2, when we pass from Zn I to Se V. It is further significant that while this increase is slow in the $4p\,{}^3P$ terms, it is much more rapid in the $5p\,{}^3P$ terms. This feature might be expected as, in addition to the effect of the increasing nuclear charge, the effect of the second electron on the " series electron " is less when the latter is in the $5p$ than when it is in the $4p$ state; in the latter case there is, therefore, a greater tendency towards the electrons behaving independently, so that the coupling tends towards the type (sl) (sl).

Term Values.

The deep triplet terms were determined by Sawyer and Humphreys by extrapolation of the Moseley diagrams, since no second terms were found in any series. Adopting the value of the $4d\,{}^3D$ term suggested by them, that of $4f\,{}^3F$ calculated from the member $4d\,{}^3D - 4f\,{}^3F$ is seen to be too high by about 16,000 cms.$^{-1}$. The terms have therefore been recalculated by the use of a Rydberg formula applied to the members of the two series $5p\,{}^3P - md\,{}^3D$ and $5p\,{}^3P - ms\,{}^3S$.

$$\begin{aligned} 5p\,{}^3P_2 - 5s\,{}^3S_1 &= -\,32157{\cdot}4 \\ - 6s\,{}^3S_1 &= 46590{\cdot}1 \end{aligned} \qquad \text{Limit } 5p\,{}^3P_2 = 151410$$

$$\begin{aligned} 5p\,{}^3P_2 - 4d\,{}^3D_3 &= -\,41352{\cdot}0 \\ - 5d\,{}^3D_3 &= 43445{\cdot}2 \end{aligned} \qquad \text{Limit } 5p\,{}^3P_2 = 152758$$

The mean value of 152084 for the limit $5p\,^3P_2$ is adopted in the estimation of the term values given in Table V.

The largest term, $4s\,^1S_0 = 404369$ cm.$^{-1}$, leads to an ionisation potential of about 49·9 volts.

Table V.—Term Values in As IV.

Term	Term value ν	$\Delta\nu$	Term	Term value ν	$\Delta\nu$
$4s\,^1S_0$	404369		$5p\,^3P_0$	153157·0	
					254·9
			$^3P_1$	152902·1	
					818·1
$4p\,^3P_0$	326557		$^3P_2$	152084·0	
		1150			
$^3P_1$	327407		$^1P_1$	150329·1	
		2530			
$^3P_2$	324877				
$^1P_1$	292347		$4f\,^3F_2$	119913	
					274
			$^3F_3$	119639	
					413
$4p^2\,^3P_0$	224435		$^3F_4$	119226	
		1534			
$^3p_1$	222901		$^1F_3$	118639	
		2926			
$^3P_2$	219975				
$^1D_2$	199711		$5d\,^3D_1$	108788·2	
					58·2
$^1S_0$	192686		$^3D_2$	108730·0	
					91·2
			$^3D_3$	108638·8	
$4d\,^3D_1$	193772·0		$^1D_2$	110534·6	
		132·8			
$^3D_2$	193639·2				
		202·8			
$^3D_3$	193436·4		$6s\,^3S_1$	105493·9	
$^1D_2$	224806		$^1S_0$	103670·1	
$5s\,^3S_1$	184241·4		α	106252	
$^1S_0$	174948·5		β	109757	
			γ	106423	

It is to be observed that the $4d\,^1D_2$ and $5d\,^1D_2$ terms are deeper than the respective triplets. Otherwise the terms appear to be perfectly regular, as indicated by the comparison of term values in the isoelectronic sequence of spectra Zn I to Se V* given in Table VI. As usual in such comparisons, the terms of As IV are divided by 16, those of Ge III by 9, and so on.

While in Zn I, Ga II and Ge III the term $5s\,^3S_1$ is larger than $4d\,^3D_3$, the reverse is the case in As IV so that a crossing of the Moseley curves for these two terms takes place after the third stage of ionisation; a corresponding feature is noticeable in the higher terms $6s\,^3S_1$ and $5d\,^3D_3$.

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* In the light of the term values of As IV now suggested, it appears that those of Se V need revision.

Table VI.—Comparison of Term Values.

Spectrum.	$4p\,{}^3\mathrm{P}_2$.	$5p\,{}^3\mathrm{P}_2$.	$5s\,{}^3\mathrm{S}_1$.	$6s\,{}^3\mathrm{S}_1$.	$4d\,{}^3\mathrm{D}_3$.	$5d\,{}^3\mathrm{D}_3$.	$4f\,{}^3\mathrm{F}_4$.
Zn I	43455	14519	22094	10334	12998	7187	6931
Ga II	29177	11683	15629	8111	12896	7069	7031
Ge III	23544	10393	13051	7030	12556	6981	[7278]
As IV	20305	9505	11515	6593	12090	6790	7452
Se V	19793	—	12094		13268		

Table VII is a list of lines of As IV and includes the list previously published by Sawyer and Humphreys. It is proposed to give a complete catalogue of the spark lines of arsenic in a future communication dealing with the analysis of As II, which is now well under way.

Table VII.—List of Classified Lines as in As IV.

λ I.A. (int.).	ν (vac.).	Classification.		
		Triplets.	Inter-combinations.	Singlets and other combinations.
4533·92 (0)	22049·8		$5s\,{}^1\mathrm{S}_0 - 5p\,{}^3\mathrm{P}_1$	
4060·69 (6)	24619·4			$5s\,{}^1\mathrm{S}_0 - 5p\,{}^1\mathrm{P}_1$
3216·14 (4)	31084·2	$5s\,{}^3\mathrm{S}_1 - 5p\,{}^3\mathrm{P}_0$		
3189·94 (6)	31339·5	${}^3\mathrm{S}_1 - {}^3\mathrm{P}_1$		
3108·81 (8)	32157·4	${}^3\mathrm{S}_1 - {}^3\mathrm{P}_2$		
2947·94 (1)	33912·1		$5s\,{}^3\mathrm{S}_1 - 5p\,{}^1\mathrm{P}_1$	
2512·18 (6)	39794·1			$5p\,{}^1\mathrm{P}_1 - 5d\,{}^1\mathrm{D}_2$
2464·00 (3)	40572·1			$5p\,{}^1\mathrm{P}_1 - \beta$
2461·43 (9)	40614·5	$4d\,{}^3\mathrm{D}_1 - 5p\,{}^3\mathrm{P}_0$		
2454·03 (10)	40737·0	${}^3\mathrm{D}_2 - {}^3\mathrm{P}_1$		
2446·06 (8)	40869·7	${}^3\mathrm{D}_1 - {}^3\mathrm{P}_1$		
2417·53 (10)	41352·0	${}^3\mathrm{D}_3 - {}^3\mathrm{P}_2$		
2406·54 (2)	41540·8		$5p\,{}^1\mathrm{P}_1 - 5d\,{}^3\mathrm{D}_1$	
2406·04 (2)	41549·4		$5p\,{}^3\mathrm{P}_2 - 5d\,{}^1\mathrm{D}_2$	
2405·73 (6)	41554·8	${}^3\mathrm{D}_2 - {}^3\mathrm{P}_2$		
2403·15 (3)	41599·4		$5p\,{}^1\mathrm{P}_1 - 5d\,{}^3\mathrm{D}_2$	
2398·04 (2)	41688·0	${}^3\mathrm{D}_1 - {}^3\mathrm{P}_2$		
2361·78 (2)	42328·0			$5p\,{}^3\mathrm{P}_2 - \beta$
2308·99 (1)	43295·8	$5p\,{}^3\mathrm{P}_2 - 5d\,{}^3\mathrm{D}_1$		
2308·19 (3)	43310·6		$4d\,{}^3\mathrm{D}_2 - 5p\,{}^1\mathrm{P}_1$	
2305·88 (5)	43354·0	${}^3\mathrm{P}_2 - {}^3\mathrm{D}_2$		
2301·15 (2)	43443·2		$4d\,{}^3\mathrm{D}_1 - 5p\,{}^1\mathrm{P}_1$	
2301·04 (9)	43445·2	${}^3\mathrm{P}_2 - {}^3\mathrm{D}_3$		
2276·90 (3)	43905·8			$5p\,{}^1\mathrm{P}_1 - \gamma$
2268·06 (4)	44076·9			$5p\,{}^1\mathrm{P}_1 - \alpha$
2266·13 (5)	44114·4	${}^3\mathrm{P}_1 - {}^3\mathrm{D}_1$		
2263·17 (9)	44172·1	${}^3\mathrm{P}_1 - {}^3\mathrm{D}_2$		
2253·11 (8)	44369·3	${}^3\mathrm{P}_0 - {}^3\mathrm{D}_1$		
2189·29 (0)	45662·7			
2146·70 (5)	46590·1	$5p\,{}^3\mathrm{P}_2 - 6s\,{}^3\mathrm{S}_1$		
2142·53 (4)	46659·0			$5p\,{}^1\mathrm{P}_1 - 6s\,{}^1\mathrm{S}_0$
2108·66 (4)	47408·4	${}^3\mathrm{P}_1 - {}^3\mathrm{S}_1$		
2097·40 (3)	47662·9	${}^3\mathrm{P}_0 - {}^3\mathrm{S}_1$		

Table VII.—(Continued).

λ (vac.).	ν (vac.).	Classification.		
		Triplets.	Inter-combinations.	Singlets and other combinations.
1480·61 (9)	67540			$4p\,^1P_1 - 4d\,^1D_2$
1473·21 (1)	67879	$4p^2\,^3P_2 - 5p\,^3P_2$		
1472·55 (1)	67909		$4p\,^1P_1 - 4p^2\,^3P_0$	
1440·00 (2)	69444		$^1P_1 - {}^3P_1$	
1435·86 (4)	69645		$4p^2\,^3P_2 - 5p\,^1P_1$	
1390·72 (0)	71905		$4d\,^1D_2 - 5p\,^3P_1$	
1381·76 (6)	72371		$4p\,^1P_1 - 4p^2\,^3P_2$	
1375·07 (10)*	72724		$4d\,^1D_2 - 5p\,^3P_2$	
[1360·34]	73511	$4d\,^3D_3 - 4f\,^3F_2$		
1356·36 (2)	73727	$^3D_2 - {}^3F_2$		
1355·06 (2)	73798	$^3D_3 - {}^3F_3$		
1353·93 (6)	73859	$^3D_1 - {}^3F_2$		
1351·34 (7)	74001	$^3D_2 - {}^3F_3$		
1347·51 (9)	74211	$^3D_3 - {}^3F_4$		
1342·69 (7)	74477			$4d\,^1D_2 - 5p\,^1P_1$
1336·80 (0)	74806		$4d\,^3D_3 - 4f\,^1F_3$	
1333·18 (2)	75009		$^3D_2 - {}^1F_3$	
1299·34 (10)	76962		$4s\,^1S_0 - 4p\,^3P_1$	
1079·49 (7)	92636			$4p\,^1P_1 - 4p^2\,^1D_2$
1003·40 (8)	99661			$4p\,^1P_1 - 4p^2\,^1S_0$
999·46 (2)	100054		$4p^2\,^3P_2 - 4f\,^3F_3$	
999·25 (9)	100075		$4p\,^3P_2 - 4d\,^1D_2$	
980·58 (10)	101981†	$4p\,^3P_2 - 4p^2\,^3P_1$		
974·61 (9)	102605		$4p\,^3P_1 - 4d\,^1D_2$	
971·13 (10)	102973†	$^3P_1 - {}^3P_0$		
956·87 (9)	104507†	$^3P_1 - {}^3P_1$		
953·25 (8)	104904†	$^3P_2 - {}^3P_2$		
946·45 (9)	105658†	$^3P_0 - {}^3P_1$		
941·91 (5)	106167			$4d\,^1D_2 - 4f\,^1F_3$
930·80 (8)	107435†	$^3P_1 - {}^3P_2$		
925·04 (1)	108103		$4p\,^1P_1 - 5s\,^3S_1$	
892·68 (10)	112022†			$4s\,^1S_0 - 4p\,^1P_1$
851·74 (10)	117407			$4p\,^1P_1 - 5s\,^1S_0$
762·75 (4)	131105†	$4p\,^3P_2 - 4d\,^3D_1$		
761·99 (8)	131235†	$^3P_2 - {}^3D_2$		
760·80 (10)	131441†	$^3P_2 - {}^3D_3$		
748·33 (8)	133631†	$^3P_1 - {}^3D_1$		
747·57 (9)	133767†	$^3P_1 - {}^3D_2$		
741·93 (8)	134784†	$^3P_0 - {}^3D_1$		
711·07 (8)	140633†	$4p\,^3P_2 - 5s\,^3S_1$		
698·50 (7)	143164†	$^3P_1 - {}^3S_1$		
692·94 (5)	144313†	$^3P_0 - {}^3S_1$		
655·88 (0)	152467		$4p\,^3P_1 - 5s\,^1S_0$	
550·03 (1)	181808			$4p\,^1P_1 - 5d\,^1D_2$
537·07 (3)	186092			$4p\,^1P_1 - a$
530·31 (2)	188569			$4p\,^1P_1 - 6s\,^1S_0$
[462·77]	[216089]	$4p\,^3P_2 - 5d\,^3D_1$		
[462·65]	[216147]	$^3P_2 - {}^3D_2$		
[462·45]	[216238]	$^3P_2 - {}^3D_3$		
[457·42]	[218619]	$^3P_1 - {}^3D_1$		
[457·30]	[218677]	$^3P_1 - {}^3D_2$		
[455·82]	[219383]	$4p\,^3P_2 - 6\mathrm{s}\,^3S_1$		
[455·02]	[219769]	$4p\,^3P_0 - 5d\,^3D_1$		
[450·63]	[221913]	$4p\,^3P_1 - 6s\,^3S_1$		
[448·30]	[223063]	$^3P_0 - {}^3S_1$		

* Coincident with a strong line of As II.

† Identifications by Sawyer and Humphreys. Bracketed lines are calculated.

Summary.

About 60 lines in the spectrum of trebly-ionised arsenic have been newly classified. The spectrum is built up from triplet and singlet terms, the absolute values of which have been determined with the aid of two members of each of the sharp and diffuse series of triplets. The ionisation potential, corresponding to the largest term, $4s\,^1S_0 = 404369$ cm.$^{-1}$, is found to be about 49·9 volts.

In conclusion, the author wishes to express his great indebtedness to Professor A. Fowler and Professor M. Siegbahn for their stimulating interest and encouragement in the course of this investigation. His thanks are due also to the Andhra University and the Madras Government for the award of a scholarship.

The Field of Force and the Form of the Carbon Dioxide Molecule.

Part I. *Thermal Diffusion in Mixtures Containing Carbon Dioxide.*

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Introduction.

All experimental workers on thermal diffusion* have examined mixtures containing carbon dioxide. We find, however, that mixtures containing this gas still appear to present novel and interesting features. An account of these special features will be given in this work.

In a previous series of experiments it was found that k_t, the ratio of the coefficient of thermal diffusion to the coefficient of ordinary diffusion, generally tends to decrease gradually at low temperatures. We decided, therefore, to make further experiments with the object of finding whether any change in k_t also occurred at high temperatures. The original intention was to make a general survey of a number of gas mixtures working up to about 750° C. or 1000° C. After this work was begun Lugg published an account of his experiments showing that k_t for a mixture of hydrogen and carbon dioxide is greater at high temperatures than it is at ordinary temperatures. This contribution to the subject furnished a valuable connection between the results obtained by Elliott and Masson and the lower results we had previously obtained using a smaller range of temperature. From his results Lugg concluded that there is a gradual increase in k_t as the temperature is raised.

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* *Cf.* 'Proc. Phys. Soc.,' vol. 43, p. 142 (1931), where full references are given to theory and experiments.

In the course of our work at high temperatures we examined a mixture of hydrogen and carbon dioxide and found that there appeared to be a sharp change, rather than a gradual change, in the value of k_t for this mixture at a definite temperature. This rather unexpected result suggested the possibility of a sharp change occurring in the nature of the forces operating during intermolecular collisions. The need for a careful investigation of this interesting possibility was apparent and we decided to concentrate on this aspect of the work, before dealing with the more general investigation of the effect of high temperatures.

Method of Experiment.

In our earliest work on thermal diffusion a continuous flow of gas was maintained through the diffusion apparatus, and the gas was drawn off for examination from the hot and cold sides. The heat was supplied by a current passing through a platinum helix. While the method served to demonstrate certain aspects of the effect, it was unsuitable for making measurements of k_t because the hot and cold regions were not clearly defined. In subsequent experiments a vessel of considerable capacity was maintained at temperatures up to about 300° C. This vessel was joined by a short connecting tube to a katharometer, the cell of which served as the small cold side of the apparatus. This form of apparatus was useful for making a rapid survey of a number of gas mixtures, but the arrangement presents a number of difficulties which may introduce serious errors at high temperatures. Thus it is difficult to screen the katharometer from the effects of the hot side, and any small change in its temperature will affect the readings of the instrument. In addition, it is difficult to maintain a vessel of considerable capacity at a uniform high temperature. We decided therefore to attempt to devise a method which would require only a small hot side and which would allow the katharometer to be at some distance from the heating apparatus.

General Principle of Method.—A diagram of the apparatus is shown in fig. 1. A continuous and fairly rapid stream of the gas mixture was maintained through the tube AB of internal diameter 0·5 cm. Leading from this tube was a silica glass side tube C, of length 5 cm. and internal diameter 0·8 cm.

The upper portion of this side tube was maintained at a uniform temperature by means of the electric furnace D. If there is no flow of gas through this side tube it will form a " pocket " and the gas in it will soon reach a steady state owing to thermal diffusion. The concentration of the gas in the pocket will differ from that of the gas in the main stream. When the steady state is reached the concentration of the gas in the main stream will be unaffected by the gas in the pocket. In practice a very slow flow of gas was maintained through the side tube, leaving it by means of the fine capillary tube EF, which had a diameter of about 0·01 cm. at its lower end. When the quantity of gas flowing through C is very small, the thermal separation can be regarded as practically complete. The gas after passing through the fine capillary tube which takes it clear of the furnace, was led through about 10 cm. of ordinary capillary tubing to the katharometer* for analysis. The katharometer could in this case be shielded from the effects of the furnace.

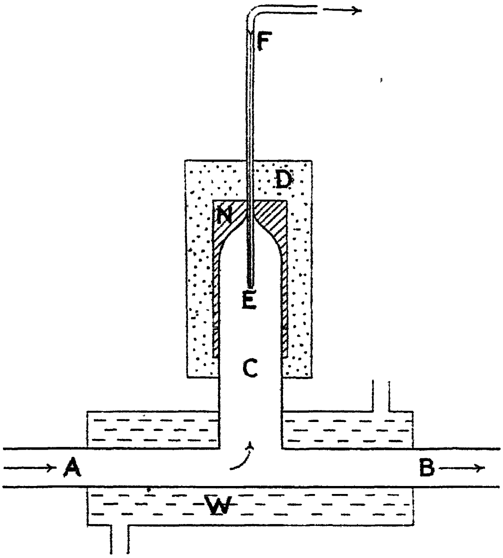

Fig. 1.—Diagram of Apparatus.

A fine capillary tube is used so that although the quantity flowing is small, the velocity of flow through the tube is comparatively great. With the slowest flow employed in the experiments, the gas travelled through this capillary with a velocity of about 7·5 cm. per second. This velocity avoids the possibility of thermal diffusion again affecting the concentration of the mixture as it passes outwards down the temperature gradient. It is important that the small sample of gas reaching the katharometer should have the same concentration as the gas in the upper part of the tube C.

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* This instrument was kindly lent by Dr. G. A. Shakespear.

With a small but definite flow of gas through the hot tube C, there will be a small change in the concentration of the gas in the main stream reaching B. This change in the main stream will be in the opposite direction to that in the gas from the hot side, and we should expect the changes of concentration in the two streams to be inversely proportional to their rates of flow. This was examined experimentally and found to be the case. The total thermal separation is the difference in the concentration between the gas in the two streams.

Further Details of Method and Apparatus.—To operate this method successfully the rates of flow of the gas mixture through the different parts of the apparatus must be effectively controlled. The gas mixture was stored in a steel cylinder under pressure. To obtain satisfactory control of the flow was a matter of considerable experimental difficulty. By means of overflow tubes dipping into liquids, thus giving constant pressure heads, both the actual pressure of the gas in the apparatus and the rate of flow through the apparatus could be controlled independently. All gas bubbles escaping through the liquids had to be small, to avoid fluctuations of pressure and flow. The rates of flow of gas in the main stream and in the hot side stream were in all cases measured by observing the times required for given volumes to collect in measuring tubes over water or acetic acid. The apparatus as finally used would give a steady flow for hours. The details of the rather complex arrangements required to maintain a uniform flow need not be given here.

The usual procedure was as follows. All the apparatus was first flushed out thoroughly with the mixture. The tube C was then raised to the required temperature by means of the furnace, and the rates of flow adjusted. In all cases the volume flowing in the main stream was at least 50 times greater than the volume flowing through the side tube in the same time. The rates of flow were then measured as described. The rate of flow through the hot tube was small; in some cases not more than 1 c.c. in 30 minutes. This means that it takes a considerable time for the gas in the katharometer cell to be flushed out, and thus attain the same concentration as the gas on the hot side. The gas in the main stream was then diverted to pass through the katharometer and the rates of flow adjusted to be the same as before. This enabled the small change in concentration of the gas in the main stream to be obtained, and the total separation could then be calculated.

Additional control experiments were made to test whether the separation could be regarded as complete. It was found that considerable variation in the rate of flow at constant furnace temperature produced no variation in the amount of separation obtained, so that the rates of flow employed could be regarded as giving practically complete separation.

This form of apparatus was not suitable for making rapid measurements. Much manipulation was required, and only one or two measurements of thermal diffusion could be obtained in one day. There was, however, considerable gain in accuracy, and in particular errors in measuring the separation at high temperatures could be avoided.

A suitable furnace was required to heat the upper portion of the side tube C to a very nearly uniform temperature. It was desirable that below this uniform region, the temperature should fall off as rapidly as possible, so that the steep temperature gradient would produce rapid thermal diffusion. Several different types of furnace were tried. Finally a nickel cylinder N (fig. 1) was drilled to fit closely round the upper end of the glass tube, the capillary tube EF projecting through a hole in the top end of the cylinder. Two layers of "ni-chrome" wire, insulated by mica, were wound on the nickel cylinder. A separate winding was made on a nickel ring which was placed on the tube just below the cylinder and insulated from it. This assisted considerably in obtaining the uniform region and the steep temperature gradient. The temperature of the inside of the tube was examined by means of a platinum and platinum-rhodium thermocouple. The windings and currents were adjusted until a length of about 3 cm. at the top of the tube could be maintained at nearly uniform temperatures over a considerable range. The capillary tube EF was arranged to project a distance of about 1·5 cm. into the tube C as shown in fig. 1, so that the gas drawn off should be taken from a region of known uniform temperature. When the apparatus was in use the thermojunction was placed near the point E. The furnace was designed for work up to about 750° C., but in making the present measurements it was not generally used above 300° C. The water jacket W, supplied from the mains, surrounded the tube carrying the main stream of gas and served to shield this tube from the heating effect of the furnace. The temperature of the water jacket gave T_2. In addition lead tubing, through which water was flowing, was wound round C immediately below the furnace. This helped to obtain a steep temperature gradient.

It is necessary to consider whether any partial separation of a gas mixture can be obtained by merely passing it through a fine capillary tube. A series of preliminary experiments were made to examine this possibility, the details of which need not be given. The gas mixture was passed through a capillary tube of length 8 cm. and internal diameter 0·01 cm. and no change in concentration could be observed. It was concluded that any small change in concentration which may occur owing to the passage through the fine tube must be considerably less than the possible error in our thermal diffusion measurements.

Experimental Results.

In the course of this work four pairs of gases were examined : hydrogen and carbon dioxide, nitrogen and carbon dioxide, hydrogen and nitrogen, hydrogen and argon. The two pairs not containing carbon dioxide were included so that the behaviour of these mixtures could be compared with the behaviour of mixtures containing carbon dioxide. It is convenient to plot the results in the form of graphs showing the relation between thermal separations as ordinates, and $\log_{10}(T_1/T_2)$ as abscissæ ; T_1 being in this case the absolute temperature of the hot side and T_2 that of the cold side. The cold side temperature is practically constant for any mixture, while the hot side temperature is varied by means of the furnace. The slope of the curve at any point is proportional to the value of k_t in a region where the temperature is T_1, for

$$k_t = \frac{d\lambda_2}{d(\log T)}$$

where λ_2 is the proportion of the lighter gas in the mixture. Thus numerical values of k_t for different temperatures can be obtained from the slope of the curves.

Using Chapman's formulæ, an expression can be obtained for k_t for a pair of gases, as a function of the proportions of the gases in the mixture, the molecules being regarded as rigid elastic spheres. From this expression theoretical values of k_t can be calculated and we can thus obtain a thermal separation ratio R_t where

$$R_t = \frac{k_t \text{ experimental}}{k_t \text{ rigid elastic spheres}}.$$

This ratio, which appears to be nearly independent of the proportions of the gases, is of special interest as the theory shows that its value depends upon the nature of the forces operating between unlike molecules during collisions.

Hydrogen and Carbon Dioxide.—Experiments were made on two mixtures of this pair of gases, containing respectively 46·9 per cent. and 34·0 per cent. of carbon dioxide. When the results for the first mixture were plotted as described, it was found that there was a sharp change in the slope of the graph at a point corresponding to a value of $T_1 = 144°$ C. With T_2 about 12° C. and T_1 having values up to 300° C. the graph obtained consisted of two intersecting straight lines, the slope of the line for the higher temperatures being greater than that for the lower temperatures. Thus in this range of temperature there is one value of k_t below 144° C., and another greater value above it.

By using Chapman's formulæ and inserting numerical values* for hydrogen and carbon dioxide mixtures we obtain

$$k_t = \tfrac{5}{2}\left\{\frac{0\cdot216\,\lambda_1 + 0\cdot139\,\lambda_2}{1\cdot275 + 1\cdot409\,\lambda_1/\lambda_2 + 0\cdot232\,\lambda_2/\lambda_1}\right\}$$

where λ_1 and λ_2 are the proportions of the heavier and lighter gases respectively in the mixture.

The following table shows the considerable increase in value which occurs in k_t, and consequently in R_t, at about 144° C.

Table I.—Values of k_t and R_t for H_2–CO_2. (First mixture, 46·9 per cent. CO_2).

	k_t experimental.	k_t rigid elastic spheres.	$R_t = \dfrac{k_t \text{ experimental}}{k_t \text{ rigid elastic spheres}}$.
Below 144° C.	0·0665	0·1575	0·422
Between 144° C. and 300° C.	0·0939	0·1575	0·596

As the temperature T_1 rose above 300° C. this mixture showed a small gradual increase in the value of k_t, the line in the graph beginning to bend upwards. This change, which is of quite a different character from the one we have been describing, requires further careful investigation before it can be properly discussed. It is probably related to the gradual falling off in the value of k_t which we have observed at low temperatures. We need only mention here that at 470° C., $k_t = 0\cdot1045$ and $R_t = 0\cdot663$.

A second mixture of hydrogen and carbon dioxide was examined to investigate the sharpness or otherwise of the change in k_t. The proportions of the two gases in this mixture were chosen so that the small apparent change in k_t, which occurs as the result of the change in concentration of the gas, would tend to make the curve bend downwards at the higher temperatures. Any change of this kind could not then be confused with the upward bending which would be due to a real increase of k_t. For this mixture 15 measurements were made with the values of T_1 from 46° C. to 306° C. The observations were made at close intervals of temperature, with special grouping in the region about $T_1 = 140°$ C. The results are shown in fig. 2, and it will be seen that a definite change occurs in the slope of the line at the point B. This change is found to be at about $T_1 = 145°$ C. which is in good agreement with the previous observation. There seems to be no indication of a curve joining the two straight lines AB and BC, so that the change can be regarded at present as a sharp one. If the change does not occur suddenly in the gas at a definite temperature, then the range of temperature in which it takes place must be a small one. A further investigation of this would be interesting.

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* The values of the molecular diameters used in this work are taken from Jeans' "Dynamical Theory of Gases" (3rd edition), p. 327, first column of table.

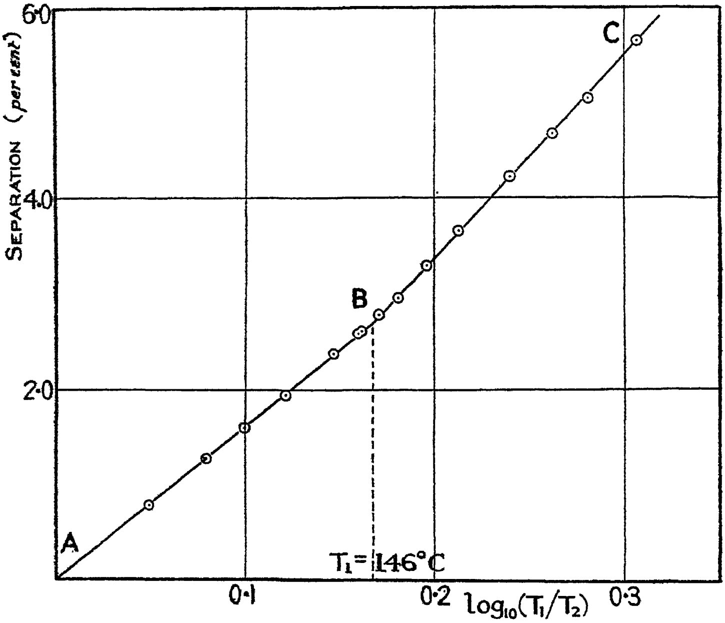

Fig. 2.—Thermal Diffusion. Hydrogen and Carbon Dioxide (2nd mixture).

The experimental value of k_t above 145° C. would be somewhat increased by making a correction for the change which occurs in k_t owing to change in

Table II.—Values of k_t and R_t for H_2–CO_2. (Second mixture, 34·0 per cent. CO_2.)

	k_t experimental.	k_t rigid elastic spheres.	$R_t = \frac{k_t \text{ experimental}}{k_t \text{ rigid elastic spheres}}$.
Below 145° C.	0·0695	0·1685	0·415
Between 145° C. and 300° C.	0·0929	0·1685	0·552

concentration. The values of R_T can, therefore, be regarded as being in satisfactory agreement with those obtained for the first mixture.

The change which occurs in k_t at about 145° C. indicates a change in the nature of the forces operating between the molecules of hydrogen and carbon dioxide during their encounters. This suggests that a change must occur in the field of force of either the carbon dioxide or the hydrogen molecules at about 145° C. Such a change in field would probably be due to a change in the molecular structure of one of the gases. In an attempt to decide whether it is the hydrogen or the carbon dioxide which is responsible for the change in k_t, we must mix each of these gases with other gases and observe the thermal diffusion effect.

Nitrogen and Carbon Dioxide.—The mixture examined contained 49·4 per cent. of carbon dioxide. The separation obtained for mixtures of this pair is less than for mixtures of hydrogen and carbon dioxide and the time taken to reach the steady state is considerably longer. The probable error in the measurements is therefore greater than in the previous experiments. As the separation is in this case small the effect of the change in concentration on the value of k_t need not be considered. Nine observations were made on the mixture, and when plotted they gave a graph consisting of two intersecting straight lines AB and BC, shown in fig. 3. The point of singularity at B corresponds to a temperature of about $T_1 = 144°$ C. This can only be regarded as accurate to within a few degrees, but it is satisfactory to find such good agreement with the temperature at which k_t changes in mixtures of hydrogen and carbon dioxide.

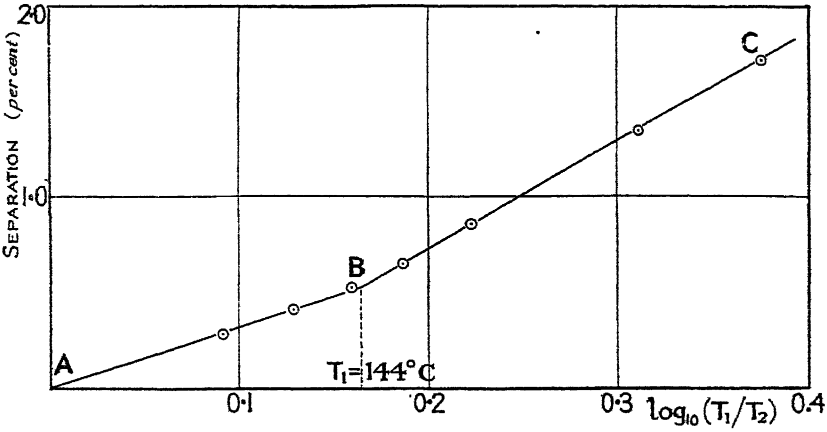

FIG. 3.—Thermal Diffusion. Nitrogen and Carbon Dioxide.

By using Chapman's formulæ and inserting numerical values for nitrogen and carbon dioxide mixtures we obtain

$$k_t = \tfrac{5}{2}\left\{\frac{0\cdot163\,\lambda_1 + 0\cdot167\,\lambda_2}{3\cdot38 + 2\cdot154\,\lambda_1/\lambda_2 + 1\cdot480\,\lambda_2/\lambda_1}\right\}$$

The values of k_t and R_T are shown in Table III.

Table III.—Values of k_t and R_T for N_2–CO_2. (49·4 per cent. CO_2.)

	k_t experimental.	k_t rigid elastic spheres.	$R_T = \dfrac{k_t \text{ experimental}}{k_t \text{ rigid elastic spheres}}$.
Below 144° C.	0·0140	0·0564	0·247
Above 144° C.	0·0247	0·0564	0·441

As we should expect, the values of R_T for nitrogen and carbon dioxide mixtures are definitely lower than the values we obtained for hydrogen and carbon dioxide mixtures, both above and below 144° C. This is due to the fact that the hydrogen molecule is harder than the nitrogen molecule.

As the change in k_t occurs at approximately the same temperature in both mixtures of hydrogen and carbon dioxide and of nitrogen and carbon dioxide, it suggests that the change in the two cases is due to the same cause. Carbon dioxide is common to both mixtures and it is reasonable to suppose that this gas is responsible for the peculiarity in k_t.

Hydrogen and Nitrogen: Hydrogen and Argon.—These two mixtures not containing carbon dioxide were examined with the same apparatus over the same range of temperature. The results when plotted gave no indication of a sharp change occurring in the value of k_t. This supports our conclusion that the effect observed in the previous mixtures is due to the presence of carbon dioxide. As the mixtures not containing carbon dioxide showed no unusual features the results for them need not be given here.

The gases used in all the experiments were taken from cylinders as supplied commercially. There is no reason to suppose that the small quantity of impurity in the carbon dioxide would produce the observed change in k_t.

Fenning and Tizard* have measured the dissociation of carbon dioxide at high temperatures and have obtained a relation between the dissociation and the temperature. Their results show that in the range of temperature we are considering the effect of dissociation would be negligible.

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* 'Proc. Roy. Soc.,' A, vol. 115, p. 318 (1927).

Tables of results for the mixtures containing carbon dioxide are given at the end of the paper so that they may be available if required for the purpose of calculation.

Discussion.

Our own early experiments* on thermal diffusion were not sufficiently accurate to show the sharp change which occurs in k_t for carbon dioxide mixtures. Although there were some indications in them of such a change, the effect at the time appeared likely to be due to experimental error.

Comparison with Observations at Low Temperatures.—In our work at low temperatures† it was shown that the value of k_t for mixtures of hydrogen and carbon dioxide could be regarded as constant from about 12° C. down to the liquefying point of carbon dioxide. It is interesting to compare the values of R_t for these low temperature observations with the values now obtained between 12° C. and 145° C. The three mixtures examined at low temperatures contained respectively 81·6, 66·0 and 54·8 per cent. of carbon dioxide, and the results yield the values of R_t, 0·459, 0·419, and 0·435. The two values of R_t now obtained between 12° C. and 145° C. are 0·422 and 0·415. Thus the measurements of R_t over the two ranges of temperature are in reasonable agreement. The two sets of observations can therefore be regarded as continuous, and we can consider R_t to be constant from —78° C. to 145° C. This agreement appears even more satisfactory when we remember that different types of diffusion apparatus were employed in the two series of experiments.

Comparison with Lugg's Observations.—Lugg‡ used a mixture containing 53·2 per cent. of hydrogen and 46·8 per cent. of carbon dioxide, with the cold side at 29° C. and the hot side at temperatures between 100° C. and 470° C. The experimental values of k_t were obtained by calculating the mean values over different temperature ranges above 29° C. With the hot side at 100° C. and at 204° C. Lugg's results give a value of R_T of about 0·46. For higher temperatures R_T shows a gradual increase to 0·57. If, however, Lugg's results are plotted in the same way as our own, they yield a graph which can similarly be regarded as made up of two intersecting straight lines AB and BC having different slopes, as shown in fig. 4. The apparent gradual increase in k_t reported by Lugg is due to the method of taking an average value over a range of temperature. Lugg's results are therefore in agreement with ours in giving two values of k_t with indications of a sharp change in value from one to the other. The point of intersection of the lines gives the temperature T_1 at which k_t changes as 204° C. This is considerably higher than the temperature we obtain for the change in k_t. It should, however, be pointed out that

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* 'Proc. Roy. Soc.,' A, vol. 99, p. 385 (1921), and A, vol. 107, p. 470 (1925).

† 'Proc. Phys. Soc.' (1929), *loc. cit.*

‡ J. W. H. Lugg, 'Phil. Mag.,' vol. 8, p. 1019 (1929).

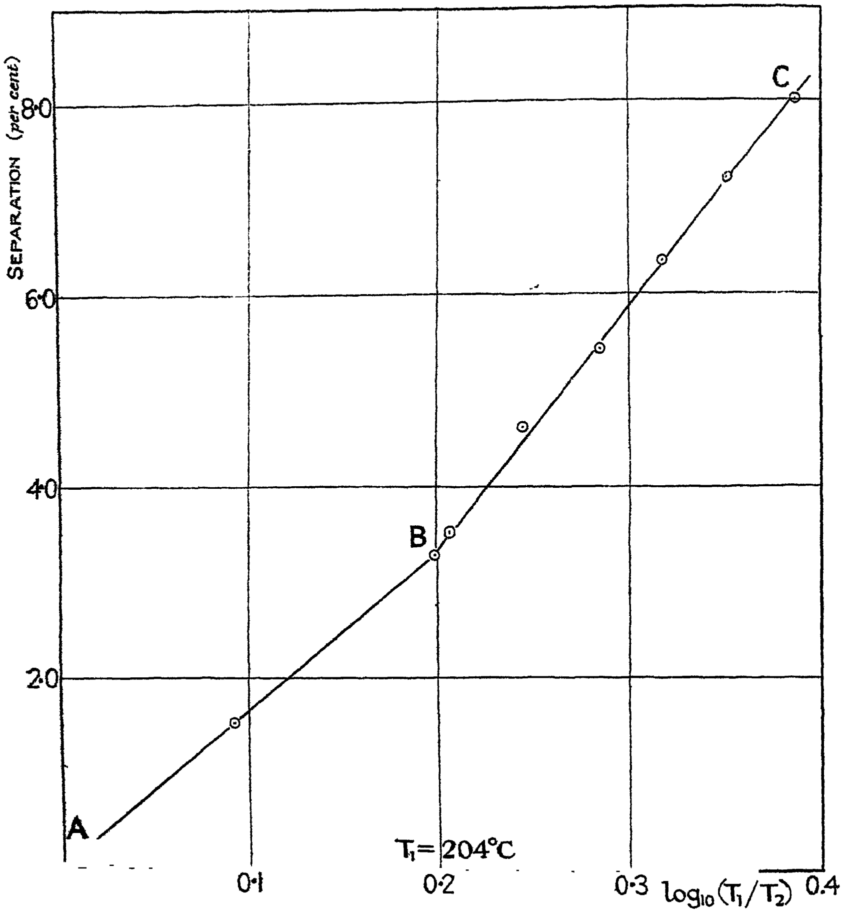

FIG. 4.—Thermal Diffusion. Lugg's Results. Hydrogen and Carbon Dioxide.

Lugg's results give only two points on the lower portion of the graph and that a comparatively small change in slope may cause a considerable difference in the point of intersection.

Lugg's results when examined in the way described give the following values of k_t and R_t (see Table IV).

These values of k_t and R_t are somewhat greater than those given by our first mixture which contained practically the same proportions of the two gases (see Table I). As already mentioned at 470° C. we obtain for this mixture

Table IV.—Values of k_t and R_t for H_2–CO_2 from Lugg's Experiments. (46·8 per cent. CO_2.)

	k_t experimental.	k_t rigid elastic spheres.	$R_t = \frac{k_t \text{ experimental}}{k_t \text{ rigid elastic spheres}}$.
Below 204° C.	0·0715	0·1575	0·458
Between 204° C. and 470° C.	0·1108	0·1575	0·703

$k_t = 0{\cdot}1045$ and $R_t = 0{\cdot}663$. When we keep in mind the experimental difficulties of the work we can consider the general agreement which is now being reached as satisfactory.

Comparison with the Observations of Elliott and Masson.—Elliott and Masson* have measured the thermal separation in mixtures of hydrogen and carbon dioxide, helium and carbon dioxide, and hydrogen and helium, using $T_1 = 490°$ C. and $T_2 = 0°$ C. Average values of k_t over this range of temperature were deduced, which give as the respective values of R_t for the three pairs 0·614,† 0·78 and 0·72. The values of R_t for hydrogen and carbon dioxide appeared at the time of publication to be unexpectedly high, being considerably greater than the value we had previously obtained using a lower range of temperature. Our present work, showing the variation in k_t, brings the results into much more reasonable agreement. Thus the high values reported by Elliott and Masson can be regarded as essentially due to the change which occurs in k_t. The serious discrepancy which had apparently arisen in the measurements of different observers is in this way explained.

It is reasonable to suppose that a change in k_t will also occur in mixtures of helium and carbon dioxide giving high average values. The value of R_t found by Elliott and Masson for this pair is higher than their value for hydrogen and carbon dioxide. This is to be expected as the helium molecule is harder than the hydrogen molecule. Our own experiments‡ have demonstrated the hardness of the helium molecule and have shown that the value of R_t is increased by substituting helium for hydrogen in a mixture.

A high value of R_t is to be expected for mixtures of hydrogen and helium. Both these molecules are very hard, and no assumption of a change in k_t is required to explain the values obtained by Elliott and Masson in the range of temperature 0° C. to 490° C.

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* G. A. Elliott and I. Masson, 'Proc. Roy. Soc.,' A, vol. 108, p. 378 (1925).

† This value of R_t for $H_2 - CO_2$ is obtained by inserting the experimental value of k_t, given by Elliott and Masson for a mixture containing 60 per cent. H_2, and using the formula shown on p. 619.

‡ 'Proc. Phys. Soc." (1931), *loc. cit.* (see table, p. 153).

The Molecular Fields of Force.—The change which occurs in R_T at about 145° C. for mixtures containing carbon dioxide indicates a change in the nature of the collisions between the molecules of carbon dioxide and the other molecules in the mixture. This change is probably due to a change in the field of force surrounding the carbon dioxide molecule.

By using Chapman's theory we can calculate q, the index of the repulsive force operating between unlike molecules during collision. An exact relation* between the value of q and that of R_T is given for the special case where the ratio of the molecular masses m_1/m_2, and the ratio of the molecular diameters σ_1/σ_2, are both very large. We shall use this relation to obtain approximate values of q for the mixtures containing carbon dioxide which we have examined.

Table V.—Approximate Values of q, the Index of the Repulsive Force.

	H_2-CO_2.	N_2-CO_2
Below 145° C.	7·8	6·2
Above 145° C.	11·0	8·0

The table shows that there is a considerable change in the index of the repulsive force both for mixtures of hydrogen and carbon dioxide, and for mixtures of nitrogen and carbon dioxide.

It thus appears that there are two kinds of carbon dioxide molecule ; a "hard" kind above 145° C. and a "soft" kind below that temperature. We shall next consider whether confirmation of this may be obtained from any other phenomenon.

Tables showing Thermal Separation in Mixtures containing Carbon Dioxide.

Table VI.—Hydrogen and Carbon Dioxide. First Mixture.

46·9 per cent. CO_2. $T_2 = 13°$ C.

T_1° C.	$\log_{10} T_1/T_2$.	Separation, per cent.
53	0·057	0·84
80	0·091	1·42
99	0·111	1·72
130	0·147	2·29
141	0·165	2·60
188	0·209	3·53
226	0·242	4·20
279	0·284	5·06
403	0·373	7·17
571	0·471	9·47
707	0·536	11·13
744	0·552	11·38

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* 'Phil. Mag.,' vol. 48, p. 606 (1924).

Table VII.—Hydrogen and Carbon Dioxide. Second Mixture.
34·0 per cent. CO_2. $T_2 = 13°$ C.

$T_1°$ C.	$\log_{10} T_1/T_2$.	Separation, per cent.
46	0·049	0·80
70	0·079	1·27
86	0·099	1·60
105·5	0·121	1·95
130	0·146	2·40
140·5	0·159	2·59
140·5	0·161	2·61
150	0·171	2·79
159·5	0·180	2·97
175	0·195	3·30
191	0·212	3·68
223	0·239	4·23
249·5	0·262	4·68
272	0·281	5·06

Table VIII.—Nitrogen and Carbon Dioxide. 49·4 per cent. CO_2.
$T_2 = 12·5°$ C.

$T_1°$ C.	$\log_{10} T_1/T_2$.	Separation, per cent.
76	0·091	0·29
109	0·128	0·41
140	0·160	0·53
170	0·187	0·66
199	0·221	0·86
201	0·222	0·86
310	0·311	1·35
403	0·375	1·72
512	0·437	2·01
602	0·485	2·38

The Field of Force and the Form of the Carbon Dioxide Molecule. Part II. *The Variation of the Viscosity of Carbon Dioxide with Temperature.*

By T. L. IBBS, M.C., Ph.D., and A. C. R. WAKEMAN, B.Sc., Physics Department, University of Birmingham.

(Communicated by S. W. J. Smith, F.R.S.—Received August 25, 1931.)

Introduction.

The variation of viscosity with temperature provides another method of investigating the forces between gas molecules. Chapman* has obtained the following expression for η the coefficient of viscosity of a gas

$$\eta = 0\cdot499 \frac{m\bar{c}}{\sqrt{2}\pi\sigma^2}$$

where m = mass of molecule, $\bar{c}$ = average velocity, and σ = molecular diameter. As $\bar{c}$ is proportional to the square root of the absolute temperature T, it follows that the value of η must be proportional to $\sqrt{T}$ for a gas in which the molecules are rigid elastic spheres. For a gas in which σ decreases with rise of temperature, η will increase more rapidly than this as the temperature rises. The variation in the value of σ will depend upon the law of force between molecules.

Our experiments on thermal diffusion in carbon dioxide mixtures led to the conclusion that a definite change occurs in the field of force of this gas at about 145° C. This change should influence the viscosity of the gas, and consequently should be demonstrated by its effect on curves showing the relation between η and $\sqrt{T}$. We may expect either (*a*) a discontinuity in these curves owing to a sudden change in the effective diameters of the molecules, or (*b*) a singularity at a point in the curve where the general slope changes as a result of the change in molecular hardness.

Although a number of observers have made experiments on the viscosity of carbon dioxide, the range of temperature from about 0° C. to 250° C. in which we are specially interested, has not been investigated very closely. Obermayer† has made six measurements extending from $-21\cdot5°$ C. to $240\cdot3°$ C., and more recently Breitenbach‡ has made five measurements extending from

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* S. Chapman, 'Phil. Trans.,' A, vol. 216, p. 279 (1915).

† A. v. Obermayer, 'Wien. Ber.,' vol. 71, p. 281 (1875).

‡ P. v. Breitenbach, 'Ann. Phys. Chem.,' vol. 67, p. 803 (1899).

—20·7° C. to 302° C. On plotting the relation between η and $\sqrt{T}$ for these measurements, it was interesting to find that in neither case could a smooth curve be drawn through the points. The results for these two observers appeared to be in good agreement; but the measurements were not sufficiently numerous to enable definite conclusions to be drawn. A further investigation of the viscosity of the gas through this range of temperature seemed necessary. We therefore attempted to devise a simple method which would be capable of showing whether any peculiarity existed in the relation between viscosity and temperature for this gas. With this limited object in view many of the difficulties of obtaining accurate measurements of absolute viscosity could be avoided.

Method of Experiment.

As many observations at small intervals of temperature would probably be needed, electrical heating appeared preferable to heating by means of vapours of substances of known boiling points. A transpiration method, in which the gas was passed through a capillary tube, was employed. Instead of using a long straight capillary tube it was sufficient to pass the gas through a short tube wound in the form of a helix.*

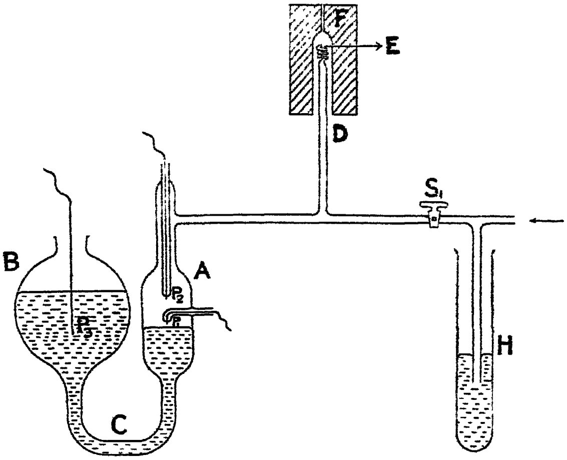

FIG. 1.—Diagram of Apparatus.

A diagram of the apparatus is shown in fig. 1. A and B are two glass vessels joined by the tube C. The vessel B of diameter about 11 cm. is open to the atmosphere; the vessel A of diameter about 4 cm. contains the gas under examination. A quantity of mercury is placed in the vessels as shown. The vessel A is joined by means of the tube D to the glass capillary tube E. The capillary tube is surrounded by the small furnace F, which was the one used in the thermal diffusion experiments. It was suitable for this work as a region of uniform temperature could be obtained over a length of about 3 cm. The capillary tube, which was about 5 cm. long, was wound into a helix of diameter 0·6 cm. and length about 0·7 cm. The diameter of the bore of the capillary was about 0·01 cm., and the external diameter about 0·1 cm. The helix could fit with ease into the upper part of the furnace. The furnace temperature was measured by means of a copper-constantan thermocouple, the junction being placed in the helix. Temperatures could be read to 0·5 of a degree.

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* The helical form was suggested to us by Mr. A. A. Dee. A helix of considerably greater dimensions has previously been used by Williams ('Proc. Roy. Soc.,' A, vol. 110, p. 141 (1926)).

The apparatus was placed in a constant temperature room, and tin plate shields were placed round the vessels A and B, and used to protect the rest of the apparatus from the effects of the small furnace. The vessel A was surrounded by cotton wool to shield it from possible draughts. The gas apparatus was all at room temperature with the exception of the helix, and the short length of tube in the furnace leading to it. This piece of tube had a length of about 3 cm. and internal volume about 0·1 c.c.

Gas from a cylinder was passed into the apparatus through the tap S_1 and the pressure in the vessel A, being greater than atmospheric, caused a difference in level of the mercury surfaces in A and B. Tap S_1 was then closed and the difference in mercury levels caused a quantity of gas to be driven from A through the capillary tube into the atmosphere. The time was taken for the mercury surface in A to move from P_1 to P_2. P_1 and P_2 are the ends of platinum wires which pass through glass tubes into A as shown in the diagram. A third platinum electrode P_3 dips into the mercury in B. When the mercury surface reached P_1 an electric circuit with P_3 was completed, a cell and telephone being placed in the circuit in series. A similar circuit was arranged in connection with P_2. With the help of this telephone arrangement, an accurate measurement of the time required by the mercury to move from P_1 to P_2 could be made by means of a stop watch.

The platinum points P_1 and P_2 had previously been cleaned, raised to a red heat, and plunged a number of times into a paste of mercury-sodium amalgam. This prevented the mercury from wetting the platinum and thus ensured a sharp contact between the points and the mercury surface. Under steady temperature conditions very consistent timings could be obtained. The same quantity of mercury was used throughout the measurements. The distance between the points P_1 and P_2 was about 1·6 cm.; the excess pressure above atmospheric in the vessel A was about 3 cm. of mercury with the level at P_1, and about 1 cm. of mercury when the level was at P_2.

The movement of the mercury from P_1 to P_2 displaces about 20 c.c. of gas out of a total volume of 80 c.c. The quantity of gas passing through the capillary tube depends chiefly on this displacement, and to a considerably less extent on the fall of pressure in the apparatus and consequent expansion of the gas. The time for a given volume of gas to pass through the capillary tube under given conditions of pressure will be proportional to its coefficient of viscosity η. The effective volume of the gas entering the capillary is its volume at the temperature of the furnace. If t is the time required for the mercury level to move from P_1 to P_2, then the coefficient of viscosity at different temperatures is approximately proportional to $t \times T_2/T_1$, where T_1 is the absolute temperature of the furnace and T_2 that of the room. We can write

$$t \times \frac{T_2}{T_1} = b\eta,$$

where b is a constant. This neglects a small correction* for changes in the barometric height.

In practice a definite excess pressure was established inside the apparatus, before the tap S_1 was closed, by means of the overflow tube H dipping into mercury. This enabled the gas to be passing through the capillary tube for some time before the mercury surface reached the point P_1, so that steady conditions could be obtained. With the telephone arrangement described, the time t could be measured with the observer outside the room and temperature disturbances could thus be avoided. The time required for the mercury level to move from P_1 to P_2 varied from about 5 minutes at room temperature to about 15 minutes at 240° C. The greatest velocity of flow in the capillary tube was about one-tenth of the critical velocity at which turbulent motion would begin in a parallel straight pipe of the same diameter.

The results of 28 observations are given in Table I in which the values of $b\eta$ are shown at different temperatures. As the bore of the tube was narrow, a correction has been made for the effect of "slip."

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* In the conditions under which these experiments were made this correction is negligible. The barometric pressure did not vary more than ± 0·5 cm. about the mean 74·8 cm.

Table I.—The Variation of the Viscosity of Carbon Dioxide with Temperature.

Temperature.	$b\eta$.	Temperature.	$b\eta$.	Temperature.	$b\eta$.
° C.		° C.		° C.	
12·5	305·0	122·5	412·7	151	438·9
13·5	305·4	128·5	418·3	154	440·9
15	306·6	133·5	423·0	176·5	460·2
52·5	345·4	136	424·8	186	468·2
69·5	362·7	137	427·3	201	479·6
96	386·8	139·5	429·2	213·5	491·5
98	390·5	142	430·9	234	506·4
107	399·5	142·5	431·6	241	514·1
114	406·3	145	434·5	249	517·6
		147	435·9		

Discussion.

When the results given in Table I were plotted as a graph showing the relation between $b\eta$ and $\sqrt{T}$ it was found that they could not be represented by one continuous curve. The best representation of the results was given by drawing two slightly curved lines with a point of singularity corresponding to a temperature of about 140° C. By drawing the graph in this way the points lay regularly on the curves. The change in general direction which occurred at the point of singularity was a small one, but on looking along the lines it could be clearly seen. As a more effective method of showing the results was subsequently found this curve need not be given here. It was found also that the combined results of Obermayer and Breitenbach could in the same way be represented by a graph consisting of two curves with a point of singularity.

During the progress of the work a careful investigation was made to find if there was an actual discontinuity between the two curves mentioned above. Observations were grouped about 140° C., but no evidence of a definite break could be obtained. This means that no considerable change in the effective diameters of the molecules accompanies the sharp change in field. A closer investigation of this interesting question would be worth while.

The Molecular Field of Force.—Measurements of the variation of viscosity with temperature have shown* that for many gases η varies approximately as a power of T, which means that the molecules can be regarded as point centres of repulsive force obeying an inverse power law. If η_1 and η_2 are the viscosities at two temperatures T_1 and T_2, then the index of the repulsive force is given by

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* *Cf.* Jeans' "Dynamical Theory of Gases," p. 283 (3rd ed.).

$$\log\left(\frac{\eta_1}{\eta_2}\right) = \frac{q+3}{2(q-1)} \log \frac{T_1}{T_2}.$$

Applying this formula to the values of $b\eta$ we have obtained at 12·5° C. and at 139·5° C. we obtain $q = 5 \cdot 7$; and similarly applying it to the values at 139·5° C. and 249·0° C. we obtain $q = 7 \cdot 8$. Thus we get satisfactory confirmation of our thermal diffusion results showing that the molecules are definitely harder over the higher range of temperature.

Similarly using Breitenbach's measurements at —20° C. and 99·1° C. we get $q = 5 \cdot 6$; and at 15° C. and 99·1° C. we get $q = 5 \cdot 5$. Using Breitenbach's values at 182·4° C. and 302° C. we get $q = 7 \cdot 5$ for the higher range of temperature.

Obermayer's viscosity measurements at —21·5° C. and at 53·5° C. give $q = 5 \cdot 4$. His measurements at 162·4° C. and at 240·3° C. give $q = 7 \cdot 0$.

C. J. Smith's* measurements of viscosity at 15° C. and 100° C. give a value of $q = 5 \cdot 4$ for the lower range of temperature.

This general agreement of a low value for q below about 140° C. and a higher value above this temperature indicates that the molecules of carbon dioxide can be regarded as point centres of repulsive force, but in this case with a change in the order of the repulsive force at that temperature. By plotting $\log \eta$ against $\log T$ we may hope to obtain a graph consisting of two straight lines having different slopes.

By plotting $\log b\eta$ against $\log T$ for our viscosity measurements we obtain the graph shown in fig. 2. This consists of the two straight lines AB and BC meeting at the point B, which corresponds to a temperature of about 140° C. The line AB has been extended in the dotted line BD, so that the difference in the slope of AB and BC may be clearly seen.

From the slope of the lines AB and BC we can obtain average values of

$$\frac{q+3}{2(q-1)},$$

and hence average values of q for the two ranges of temperature. Thus for AB we obtain $q = 5 \cdot 7$ and for BC we obtain $q = 7 \cdot 5$.

Similarly plotting $\log \eta$ against $\log T$ for the viscosity measurements of Obermayer and Breitenbach we obtain the graph shown in fig. 3, which again

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* C. J. Smith, 'Proc. Phys. Soc.,' vol. 34, p. 155 (1922).

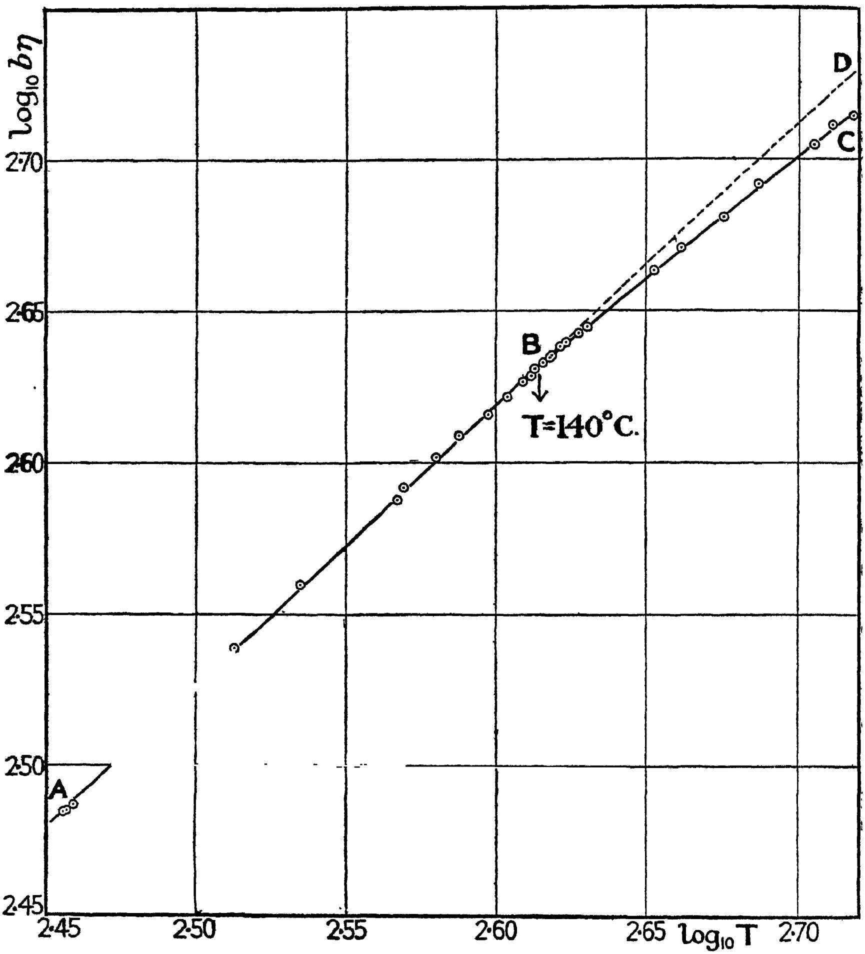

FIG. 2.—The Viscosity of Carbon Dioxide.

consists of two straight lines AB and BC of different slope; the point B corresponding to a temperature of about 140° C. This is in striking agreement with our own results, and the change in field as recorded by viscosity can be considered to be well established. In this case AB gives $q = 5 \cdot 6$, and BC gives $q = 7 \cdot 2$.

The temperature of 140° C. at which the field changes is in reasonable agreement with the temperature of 145° C. obtained by thermal diffusion. This temperature may actually be a little lower for viscosity than for thermal diffusion, but we cannot attach special significance to this small difference at present. It is suggested later that the molecule may possibly be somewhat unstable over a considerable range of temperature.

A similar investigation of nitrous oxide in thermal diffusion and viscosity is in progress.

It appears likely that the change in molecular field of carbon dioxide occurs as the result of a change in the form or the structure of the molecule. We shall next consider whether other phenomena provide any evidence of a change in form.

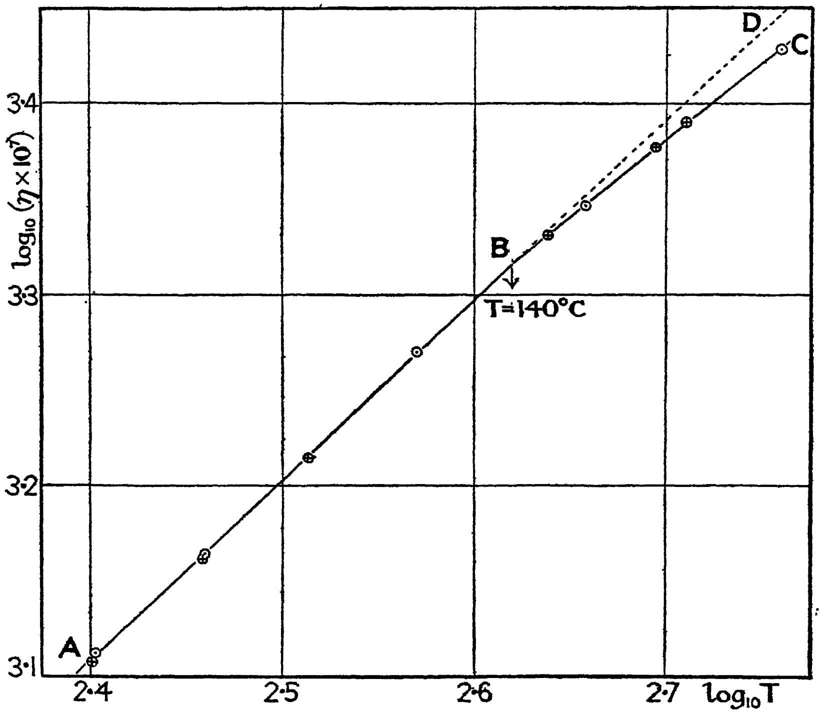

Fig. 3.—The Viscosity of Carbon Dioxide. Observations by ⊙, Breitenbach; ⊕, Obermayer.

[*Note added* 23*rd Nov.*, 1931.—Recent measurements of the viscosity of carbon dioxide by Trautz and Kurz ['Ann. Physik,' vol. 9, p. 983 (June, 1931)] can be used to give further support to our conclusion that there is a sharp change in the molecular field of the gas. Six measurements are given at temperatures between 26·9° C and 276·9° C. When these are plotted in the way shown in figs. 2 and 3, they give a graph consisting of two intersecting straight lines, with three points lying exactly on each line. The temperature corresponding to the point of intersection is about 139° C, which is in good agreement with the temperature we obtain. The values of q obtained from the slopes of the lines are $q = 5\cdot8$ and $q = 6\cdot8$.]

The Field of Force and the Form of the Carbon Dioxide Molecule.

Part III. *The Form of the Carbon Dioxide Molecule.*

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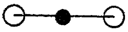
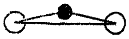
(Communicated by S. W. J. Smith, F.R.S.—Received August 25, 1931.—Revised October 14, 1931.)

Introduction.

There appears to be considerable uncertainty as to the form of the carbon dioxide molecule. Some writers consider the molecule to be of the symmetrical* "straight" type in which the three atomic nuclei are in line, thus



Others consider the molecule to be of the triangular or "bent" type, thus



The evidence for the straight or the bent form of molecule appears in some cases to be conflicting.

The behaviour of carbon dioxide in both thermal diffusion and viscosity leads to the conclusion that there is a definite change in the nature of the molecular field of the gas at about 145° C., and it is interesting to consider whether the change in molecular field is associated with a change in the form of the molecule.

The Specific Heat and Infra-red Absorption Spectrum.

If a change occurs in the form of the molecule it will probably show itself by a peculiarity in the specific heat.

It is well known that there are three strong bands in the infra-red absorption spectrum at about 4·3 μ, 2·7 μ, and 14·7 μ, corresponding to frequencies which can be denoted respectively by ν_1, ν_2 and ν_3. These are sometimes considered to be the three fundamental frequencies which would be required for a molecule of the triangular type; ν_1 being due to the oscillation of the carbon atom in the direction of the line joining the two oxygen atoms, ν_2 being due to the oxygen atoms oscillating in the same phase about the carbon atom, and ν_3 being due to the oscillation of the carbon atom perpendicular to the line joining the two oxygen atoms. Writers who consider the molecule to be of the straight type regard the oscillation of the two oxygen atoms about the carbon atom as optically inactive. They generally regard the frequencies ν_1 and ν_3 as fundamentals, and consider ν_2 to be a combination of other frequencies.

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* A third type in which the atoms are in line but with the carbon placed unsymmetrically between the two oxygen atoms has been considered by Hund, 'Z. Physik,' vol. 31, p. 81 (1924), who concludes that this form is unstable and would therefore not occur.

Thus Dennison,[*] who has extended the work of Bjerrum[†] basing his calculations on the observations of Coblentz[‡] and Barker,[§] considers the molecule to be of the triangular type. Schaefer and Philipps[||] reported a confirmation of Dennison's model from further experimental work on the absorption spectrum. On the other hand, Eucken[¶] does not regard ν_2 as a fundamental frequency and supports his case for a straight model by calculations of the specific heat which are in good agreement with observations at low and medium temperatures. Rawlins,[**] Wolf[††] and Snow[‡‡] have recently surveyed the behaviour of the gas in a number of phenomena and are all in favour of the straight model.[§§]

Special attention should be called to an interesting paper by McCrae[||||] who has suggested the possibility of a change in the form of the molecule from a bent type at high temperatures to a straight type at low temperatures. McCrae shows that Dennison's model gives a satisfactory representation of the specific heat at high temperatures, and modifies this model to account for the specific heat at low temperatures by suggesting the possibility that molecules in which

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[*] 'Phil. Mag.,' vol. 7, p. 195 (1926).

[†] 'Deuts. Phys. Ges. Verh.,' vol. 16, p. 737 (1914).

[‡] "Investigations of Infra-red Spectra," 'Carnegie Institute of Washington, D.C. (1905).'

[§] 'Astrophys. J.,' vol. 55, p. 391 (1922).

[||] 'Z. Physik,' vol. 36, p. 641 (1926).

[¶] 'Z. Physik,' vol. 37, p. 714 (1926).

[**] "Faraday Society Discussion," p. 925 (1929).

[††] 'Z. Phys. Chem.,' vol. *131*, p. *90* (*1927*).

[‡‡] 'Proc. Roy. Soc.,' A, vol. 198, p. 294 (1930).

[§§] Langmuir, 'J. Amer. Chem. Soc.,' p. 904 (1919), and Rankine, 'Proc. Roy. Soc.,' A, vol. 98, p. 309 (1921), have discussed the straight form of the CO_2 molecule from other considerations.

[||||] 'Proc. Camb. Phil. Soc.,' vol. 23, p. 890 (1927), and vol. 24, p. 290 (1928).

ν_3 is not excited are straight. In this way reasonable agreement with the specific heat at low temperatures was obtained. The change from the bent to his straight model is shown in the diagram given by McCrae to occur at a temperature below 0° C. McCrae's work has been discussed by R. H. Fowler.*

With a knowledge of the change which occurs in the molecular field of the gas at about 145° C. it becomes a matter of interest to examine the experimental data on specific heat to see whether there is any evidence for a change in specific heat at that temperature. Fig. 1 shows the relation between specific heat and temperature for carbon dioxide. The "line" AB showing the theoretical values of the specific heat at constant volume C_v for Eucken's straight model, is drawn from McCrae's calculated data. The "line" CD showing the theoretical values of C_v for Dennison's model. is also drawn from McCrae's calculated data. In his paper McCrae quotes the results of experiments which give points lying approximately along AE and ED, the temperature corresponding to the point E at which the change takes place being about 0° C. Assuming that there is a change in the form of the molecule at about 145° C., then the specific heat may follow the course A to F and G to D as shown by the thick lines, with a discontinuity in the curve between the points F and G. We shall first consider whether there is any experimental evidence for the portion of curve EF.

In his first paper dealing with the form of the carbon dioxide molecule, Eucken quotes experimental data which give strong support to his straight model up to 100° C., using the measurements of a number of observers to obtain points lying along EF. He quotes three measurements by Holborn and Henning† above 100° C. and the two higher measurements lie considerably below the value required by the straight model. Additional evidence in support of EF can be obtained from measurements by Joly,‡ Wiedemann,§ and Regnault.|| In a later paper Eucken and Lüde¶ give further experimental support for the straight model by measurements extending from —1·7° C. to 214·5° C., made by the Lummer and Pringsheim method. Difficulties appear to be encountered at the higher temperatures where large corrections have to be employed in the case of carbon dioxide.

* "Statistical Mechanics," p. 64 (1929).

† 'Ann. Physik,' vol. 23, p. 809 (1907).

‡ 'Proc. Roy. Soc.,' A, vol. 55, p. 393 (1894).

§ 'Ann. Phys. Chem.,' vol. 157, p. 1 (1876).

|| 'Mém. Acad.,' vol. 26, p. 1 (1862).

¶ 'Z. Phys. Chem.,' vol. 5, p. 413 (1929).

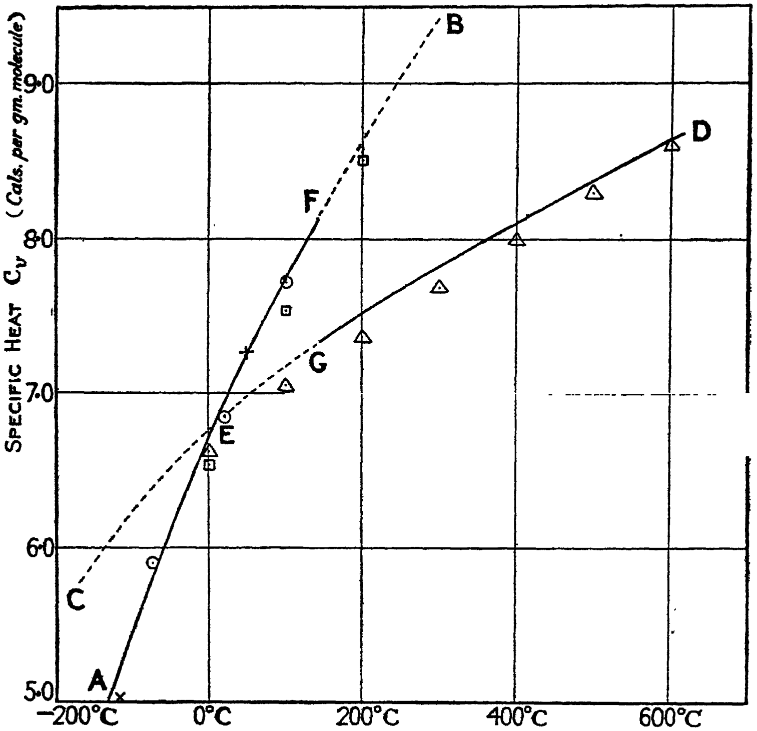

FIG. 1.—The Specific Heat of Carbon Dioxide. Observations by : △, Dixon ; ⊙, Swann, ⊙, Heuse ; ⊡, Wiedemann ; ×, Donath ; +, Joly.

The points shown in the diagram were obtained from the observations given in the following table :—

Observations of the Specific Heat of Carbon Dioxide.

Temperature ° C.	C_v cals. per gm. molecule.	Observer.
−118	5·02	Donath.*
− 75	5·90	Heuse.†
20	6·85	,,
0	6·538	Wiedemann.‡
100	7·532	,,
200	8·503	,,
20	6·849	Swann.§
100	7·721	,,
50	7·26	Joly.‖
0	6·616	Dixon.¶
100	7·049	,,
200	7·365	,,
300	7·685	,,
400	8·000	,,
500	8·203	,,
600	8·601	,,

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[*] "Discussion at the Bunsen Co., Stuttgart (1926)."

[†] 'Ann. Physik,' vol. 59, p. 86 (1919).

[‡] 'Ann. Phys. Chem.,' vol. 157, p. 1 (1876).

[§] 'Phil. Trans.,' A, vol. 210, p. 199 (1911).

[‖] 'Proc. Roy. Soc.,' A, vol. 55, p. 393 (1894).

[¶] 'Proc. Roy. Soc.,' A, vol. 105, p. 199 (1924).

The evidence furnished by measurements of specific heat at high* temperatures appears to be decidedly in favour of Dennison's model. In support of this model McCrae uses the observations of Partington and Shilling.† Dixon's (*loc. cit.*) measurements are in even closer agreement with the requirements of Dennison's model, and can be used to establish the portion of curve GD. An interesting difficulty is presented by Dixon's measurement at 100° C. which gives a point close to the dotted portion EG of the curve for the bent model. Dixon's measurements were obtained indirectly by a velocity of sound method, and the question arises as to whether this method and calorimetric methods will give different values of the specific heat of carbon dioxide in the range of temperature 0° C. to 145° C. Measurements of specific heat are known to depend to some extent on the method employed, but the difference in this case appears to be much greater than usual.

Although the experimental evidence is of a complex nature it does not appear to be opposed to the conception of a change in specific heat at about 145° C. A change in the form of the molecule at a definite temperature would probably result in a discontinuous change in the specific heat. In the diagram a change is shown from F where C_v is about 8·2 cals. per gram molecule, to G where C_v is about 7·4 cals. per gram molecule. It will be seen that the specific heat for the straight model is less than that for the bent model at temperatures below the point E where the curves cross. This means that a change in the molecules of the gas from the straight to the bent form could only occur, without the addition of " latent " heat at the temperature of change, by the specific heat rising to a maximum above E and then falling discontinuously. No further discussion of the question of energy interchange between the two forms can profitably be attempted at present.

More measurements of the specific heat of the gas are desirable. A comparison of the results obtained by calorimetric and by velocity of sound methods would be of interest.

The conception of a molecule which is normally straight between 0° C. and 145° C. but which can be regarded as rather unstable, may assist in explaining certain difficulties. Thus the three fundamental bands of a triangular molecule may appear in the ordinary infra-red absorption spectrum as a result of their excitation by absorbed energy. At any instant a few molecules only may be in the triangular form. It would be interesting to know how the intensity and structure of the three chief absorption bands vary with the temperature of the gas.

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* Temperatures above about 200° C.

† " The Specific Heat of Gases " (1924).

The Structure of Solid Carbon Dioxide.

Mark* has produced X-ray evidence which shows that the CO_2 molecules exist in the solid state, and that they are linear in form.

The Di-electric Constant.

It is generally accepted that the straight form of the molecule will be of the non-polar type, and that the bent form will be of the polar type. Observations of the variation of the di-electric constant with temperature, in conjunction with Debye's† theory, give a means of investigating the molecular polarisation. Thus Weigt‡ and Kliefoth§ report the existence of a small electric moment. Stuart|| has more recently made a number of measurements between 0° C. and 180° C. and considers that there is no electric moment. He concludes that the atoms lie in a straight line. One only of his measurements was made above 145° C., so that he is dealing chiefly with the low temperature form of the gas. An extension of these measurements to higher temperatures would be of considerable interest.

In a recent discussion Michels¶ refers to some work by Kirkwood which appears to show that at high pressures the non-polar form changes to the polar form. It is possible that this change is associated with the change under discussion and suggests that the temperature at which the form changes can be lowered by increasing the pressure.

The Raman Effect.

The Raman effect for carbon dioxide has been observed by Dickinson, Dillon and Rasetti** and discussed by Rasetti.†† No lines were observed corresponding to the absorption lines of the infra-red spectrum. The principal lines recorded were transitions 1284 $cm.^{-1}$ and 1392 $cm.^{-1}$. Rasetti points out that these correspond to the difference in frequency between the components of the double

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* 'Z. Electrochem.,' vol. 31, p. 523 (1925).

† 'Z. Physik,' vol. 13, p. 97 (1912).

‡ 'Z. Physik,' vol. 22, p. 643 (1921).

§ 'Z. Physik,' vol. 39, p. 402 (1926).

|| 'Z. Physik,' vol. 47, p. 457 (1928).

¶ A. M. J. F. Michels, quoting Kirkwood 'Proc. Roy. Soc.' A, vol. 127, p. 258 (1930).

** 'Phys. Rev.,' vol. 34, p. 582 (1929).

†† 'Nature,' vol. 123, p. 205 (1929).

band at 2·7 μ and the band at 4·25 μ. This suggests that the effect observed may be associated in some way with an optically inactive frequency, possibly ν_2. It would be of considerable interest to examine the Raman effect at temperatures above 145° C. to see whether shifts corresponding to ν_1, ν_2 and ν_3 would then appear.

Thermal Conductivity.

The kinetic theory shows that there is a relation between the thermal conductivity, the specific heat at constant volume, and the viscosity of a gas of the form

$$\kappa = a\eta C_v,$$

where κ is the thermal conductivity, η the viscosity, and a is a numerical multiplier varying for different gases. There is a change in the relation between viscosity and temperature at about 145° C., and there is also evidence to suggest a change in C_v. Chapman and Enskog have shown that the value of a, which is 2·5 or less, will depend to some extent on the nature of the forces operating between the molecules during collisions.* As a and η depend upon the law of force operating, and as C_v depends upon the form of the molecules, a detailed knowledge of the variation of κ with temperature would be of interest. The only observations at present available which extend over a considerable range of temperature were made by Stafford,† but these are not sufficiently numerous for the purpose required.

Conclusion.

The evidence afforded by thermal diffusion, viscosity, and specific heat, leads to the conclusion that the molecules of carbon dioxide are of two definite kinds depending upon the temperature. It seems probable that the "soft" low temperature molecule corresponds to a straight model, and that the "harder" high temperature molecule corresponds to a bent model.

Further investigations are desirable in a number of directions, some of which have been indicated.

Acknowledgment.

We desire to express our thanks to Professor S. W. J. Smith for the valuable help he has given by granting full facilities for this work.

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* *Cf.* Jeans' "Dynamical Theory of Gases," p. 299 (3rd ed.).

† 'Z. Phys. Chem.,' vol. 77, p. 46 (1911).

Intensity Distribution in the Band Spectrum of Helium (He_2) for the Region λ 6100—λ 6500.

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(Communicated by O. W. Richardson, F.R.S.—Received September 15, 1931.)

Introduction.

Since the discovery in 1924 by Dorgelo* that lines belonging to the same atomic multiplet often bear a simple integral relation to one another, the investigation of spectral intensities both from a theoretical and experimental standpoint has taken on a new aspect. This discovery led him, with Burger, to formulate the summation rule now known as the Summation Rule of Burger and Dorgelo† which though originally put forward to account for atomic evidence became applied, ultimately, in a modified form to band spectra.

In the hands of Fowler, Dieke, Hönl and London, Mulliken‡ and others this has led to the rapid development of theoretical intensity relations and also to a revision of quantum numeration.

For a time the theoretical predictions remained unverified except for some qualitative data, but with the improvement of the technique of intensity measurement quantitative experimental evidence is accumulating in support of the theoretical data.

Work of a quantitative nature in connection with band spectra has been carried out by a number of investigators among whom we may mention Childs, Ornstein and van Wijk, Kapuscinski and Eymers, Elliott, Fujioka§ and others. Of these Childs and Fujioka have made measurements in the band spectrum of helium, the former for the λ 4650 band and the latter for the so-called "decoupling bands." A second band, the λ 6400 band, the strong first member of the triplet system, but briefly referred to by Fujioka seemed to be of considerable importance and it is proposed in the present investigation to consider the intensity relations in this band in detail.

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* Dorgelo, 'Z. Physik,' vol. 13, p. 206 (1923); vol. 22, p. 170 (1924).

† Burger and Dorgelo, 'Z. Physik,' vol. 23, p. 258 (1924).

‡ Fowler, 'Phil. Mag.,' vol. 49, p. 1272 (1925); Dieke, 'Z. Physik,' vol. 33, p. 161 (1925); Hönl and London, 'Z. Physik,' vol. 33, p. 803 (1925); Mulliken, 'Phys. Rev.,' vol. 29, p. 391 (1927) and vol. 30, pp. 138 and 785 (1927).

§ Childs, 'Proc. Roy. Soc.,' A, vol. 118, p. 296 (1928); Ornstein and van Wijk, 'Z. Physik,' vol. 49, p. 315 (1928); Kapuscinski and Eymers, 'Z. Physik,' vol. 54, p. 246 (1929); Elliott, 'Proc. Roy. Soc.,' A, vol. 127, p. 638 (1930) and 'Diss. Utrecht' (1930); Fujioka, 'Z. Physik,' vol. 63, p. 175 (1930); Childs and Mecke, 'Z. Physik,' vol. 68, p. 344 (1931); Mecke and Childs, 'Z. Physik,' vol. 68, p. 362 (1931).

Experimental.

(*a*) *Excitation of the Helium* (He_2) *Spectrum.*—The tube used for the excitation of the helium spectrum is shown diagrammatically in fig. 1. The tube, in length about 50 cm., had a cross section of 1·5 cm. The main electrodes EE were of aluminium and a third electrode of silver was attached as shown at E′. The two ends of the main stem were closed with a mirror M and a quartz window W, both secured to the stem with sealing wax.

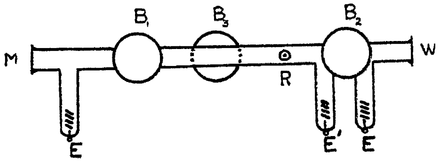

Fig. 1.

Three bulbs B_1, B_2, B_3 were fused on as shown, B_1 and B_2 containing P_2O_5 and B_3 caustic potash. A palladium regulator was attached at R. Only a very faint trace of neon, if any, was present, the helium being at from 5–10 mm. pressure.

Any water vapour present was removed by the P_2O_5 oxygen and carbon monoxide by the caustic potash and the hydrogen content could be regulated by means of the palladium regulator. The silver electrode was included as a precaution against traces of mercury vapour. The former when "spluttered" by a heavy discharge absorbs the mercury vapour. This precaution was necessary since even the slightest trace of mercury vapour gives a brilliant spectrum in the presence of helium.

The tube was excited by means of a condensed discharge generated by an alternator and transformer, the secondary of which was shunted with a condenser of a few thousand centimetres capacity. A spark gap was placed in series with the tube.

The spectrum was photographed in the first order of a 21-foot concave grating. The tube in the end-on position, was placed with the quartz window W close up to a piece of glass placed immediately in front of the slit. The glass screen was employed to eliminate the overlap of the first order spectrum by the violet end of the second order.

(*b*) *Photometric Technique.*—Unfortunately it is impossible to measure the intensities of the lines directly by means of, say, a thermocouple or photoelectric cell, for at present these instruments are not sensitive to such very small illumination. Instead the measurements have to be made from observations of the densities of the images which the lines produce on a photographic plate.

The precautions necessary and the processes employed have been indicated fully in the 'Philosophical Magazine.'* This paper will be referred to in what follows as Paper I.

The method adopted for calibrating the plates in the present case was one used extensively by Harrison† in his work on the relative intensities in atomic multiplets.

A large number of plates were obtained with spectrum and calibration marks for different times of exposure and for two different variety of plates, Ilford Rapid Panchromatic and Ilford Special Rapid Panchromatic. Each plate was developed separately in 1 : 24 Azol, washed and fixed, rewashed and rinsed before drying in distilled water.

Photometric records were obtained for the most suitable of these plates on a photoelectric recording microphotometer,‡ kindly placed at our disposal by Professor Fowler, of the Royal College of Science.

Records were obtained both for the calibration marks and also for the spectrum.

Characteristic curves were drawn for the various wave-lengths as indicated in Paper I for the whole range of the spectrum investigated. From these and the photometric record of the spectrum the relative intensity distribution in the spectrum was deduced.

Experimental Results.

The relative intensities of the band lines of the helium spectrum between λ 6100 and λ 6500 measured in the manner described above are given in Table I.

Some difficulty is usually experienced with helium tubes due to contamination with neon and although the helium contained in the present tube appeared to be free from even small traces of neon it was thought desirable to indicate the intensity values for lines which happen to coincide with a neon line. These,

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* Read and Johnson, 'Phil. Mag.,' vol. 74, p. 1152 (1931).

† Harrison, 'J. Opt. Soc. America,' vol. 18, p. 6 (1929).

‡ The new instrument constructed by the Cambridge Instrument Company.

Table I.—Relative Intensities in He_2 Spectrum for the Region λ 6100 to λ 6500.

Wave-length.	ν (vac.) approx.	Mean relative intensity.	Identification and remarks.
6514·38	15346	14	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K + 1, K = 17)
6501·02	15378	24	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K + 1, K = 15)
6487·69	15410	38	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K + 1, K = 13)
6474·49	15441	64	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K + 1, K = 11)
6465·71	15462	7	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K, K = 15)
6461·40	15472	94	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K + 1, K = 9)
6448·44	15503	123	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K + 1, K = 7)
6439·36	15525	13	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K, K = 13)
6435·66	15534	130	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K + 1, K = 5)
6423·04	15565	125	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K + 1, K = 3)
6413·87	15587	15	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K, K = 13)
6412·42	15590	18	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K, K = 17)
6410·71	15595	52	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K + 1, K = 1)
6409·44	15598	15	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K, K = 15)
6407·53	15602	47 (?)	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K − 1, K = 19)
6406·82	15604	74	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K, K = 13)
6404·57	15610	113	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K, K = 11)
6402·75	15614	162	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K, K = 9)
6401·19	15618	192	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K, K = 7)
6399·89	15621	205	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K, K = 5)
6399·25	15623	172	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K, K = 3)
6398·72	15624	85	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K, K = 1)
6391·95	15640	26	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K − 1, K = 17)
6389·50	15646	28	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K, K = 9)
6385·65	15656	11	$3d\,{}^1\Pi_b \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 14)
6381·19	15667	52	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K − 1, K = 3)
6376·79	15678	39	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K − 1, K = 15)
6369·98	15694	79	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K − 1, K = 5)
6366·59	15703	35	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K, K = 7)
6362·34	15713	57	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K − 1, K = 13)
6361·77	15715	13	$3d\,{}^1\Pi_b \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 12)
6359·19	15721	80	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K − 1, K = 7)
6348·85	15747	130 (?)	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K − 1, K = 11)
6348·84	15747	(?)	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K − 1, K = 9)
6345·63	15755	39	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K, K = 5)
6339·03	15771	(?)	$3d\,{}^1\Pi_b \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 10)
6339·02	15771	(?)	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K − 1, K = 11)
6336·42	15777	75	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K − 1, K = 9)
6329·75	15794	34	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K − 1, K = 13)
6327·74	15799	37	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K, K = 3)
6325·39	15805	74	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K − 1, K = 7)
6321·01	15816	22	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K − 1, K = 15)
6317·44	15825	25	$3d\,{}^1\Pi_b \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 8)
6316·34	15828	56	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K − 1, K = 5)
6312·89	15836	14	$3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ (K → K − 1, K = 17)
6310·27	15843	27	$3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$ (K → K − 1, K = 3)
6297·52	15875	29	$3d\,{}^1\Pi_b \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 6)
6279·53	15920	30	$3d\,{}^1\Pi_b \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 4)
6266·56	15953	20	$3d\,{}^1\Pi_a \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 9)
6263·70	15961	24	$3d\,{}^1\Pi_b \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 2)
6262·28	15964	29	$3d\,{}^1\Pi_a \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 7)
6259·67	15971	36	$3d\,{}^1\Pi_a \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 5)
6257·73	15976	35	$3d\,{}^1\Pi_a \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 3)
6255·05	15983	19	$3d\,{}^1\Pi_a \rightarrow 2p\,{}^1\Pi$ (K → K + 1, K = 1)
6235·14	16034	21	$3d\,{}^1\Pi_b \rightarrow 2p\,{}^1\Pi$ (K → K − 1, K = 2)
6229·75	16048	15	$3d\,{}^1\Pi_b \rightarrow 2p\,{}^1\Pi$ (K → K − 1, K = 14)

Table I—(continued).

Wave-length.	ν (vac.) approx.	Mean relative intensity.	Identification and remarks.
6228·27	16051	37	$3d\,^1\Pi_b \rightarrow 2p\,^1\Pi$ (K→K − 1, K = 4)
6225·53	16058	26	$3d\,^1\Pi_b \rightarrow 2p\,^1\Pi$ (K→K − 1, K = 12)
6223·60	16063	47	$3d\,^1\Pi_b \rightarrow 2p\,^1\Pi$ (K→K − 1, K = 6)
6222·42	16066	28	$3d\,^1\Pi_b \rightarrow 2p\,^1\Pi$ (K→K − 1, K = 10)
6220·53	16071	50	$3d\,^1\Pi_b \rightarrow 2p\,^1\Pi$ (K→K − 1, K = 8)
6218·15	16078	20	$3d\,^1\Pi_a \rightarrow 2p\,^1\Pi$ (K→K − 1, K = 3)
6217·80	16078	18	$3d\,^1\Pi_a \rightarrow 2p\,^1\Pi$ (K→K , K = 7)
6211·50	16095	21	$3d\,^1\Pi_a \rightarrow 2p\,^1\Pi$ (K→K , K = 9)
6207·50	16105	23	$3d\,^1\Pi_a \rightarrow 2p\,^1\Pi$ (K→K , K = 11)
6206·04	16109	20	$3d\,^1\Pi_a \rightarrow 2p\,^1\Pi$ (K→K , K = 15)
6205·76	16110	18	$3d\,^1\Pi_a \rightarrow 2p\,^1\Pi$ (K→K , K = 13)
6197·79	16130	19	$3d\,^1\Pi_a \rightarrow 2p\,^1\Pi$ (K→K − 1, K = 5)
6178·51	16181	22	$3d\,^1\Pi_a \rightarrow 2p\,^1\Pi$ (K→K − 1, K = 7)
6161·32	16230	37	$3d\,^1\Pi_a \rightarrow 2p\,^1\Pi$ (K→K − 1, K = 9)
6146·50	16265	21	$3d\,^1\Pi_a \rightarrow 2p\,^1\Pi$ (K→K − 1, K = 11)
6134·20	16298	12	$3d\,^1\Pi_a \rightarrow 2p\,^1\Pi$ (K→K − 1, K = 13)

together with lines of doubtful value due to overlap, are followed by (?). The wave-lengths have been collected from a series of papers.*

The significance of the fourth column will be evident later.

The results arranged more conveniently into their respective bands are shown in a graphical manner in fig. 2. The length of the vertical lines represent

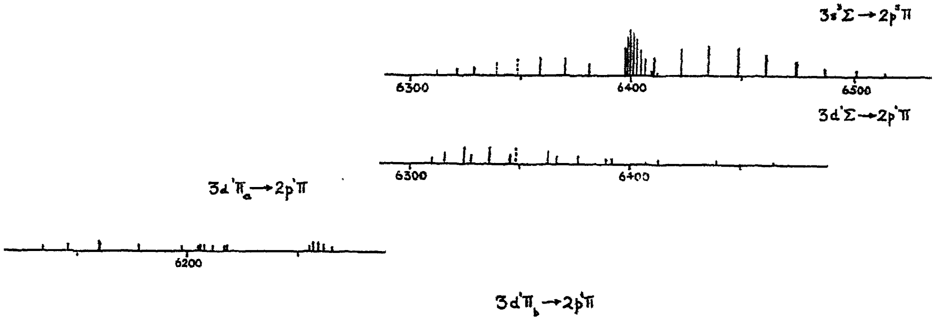

FIG. 2.—Intensities in Helium Band Spectrum (λ 6100–λ 6500).

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* Curtis, 'Proc. Roy. Soc.,' A, vol. 101, p. 38 (1922); Curtis, 'Proc. Roy. Soc.,' A, vol. 103, p. 315 (1923) and vol. 118, p. 157 (1928); Curtis and Long, 'Proc. Roy. Soc.,' A, vol. 108, p. 513 (1925); Curtis and Harvey, 'Proc. Roy. Soc.,' A, vol. 121, p. 381 (1928) and vol. 125, p. 484 (1929); Dieke, Takamine and Suga, 'Z. Physik,' vol. 49, p. 637 (1928); Dieke, Imanishi and Takamine, 'Z. Physik,' vol. 54, p. 826 (1929) and vol. 57, p. 305 (1929); Weizel and Füchtbauer, 'Z. Physik,' vol. 44, p. 431 (1927); Weizel, 'Z. Physik,' vol. 51, p. 328 (1928) and vol. 54, p. 321 (1929); Weizel and Pestel, 'Z. Physik,' vol. 56, p. 197 (1929).

their relative intensity, and the horizontal spacing the wave-lengths of the lines.

The Structure of the Band Spectrum of Helium.

During the past few years the helium band spectrum has been the subject of extensive investigation. As in the case of the molecular spectrum of hydrogen, a large number of levels have been identified.

The work of Curtis, Dieke and Weizel (see footnote p. 647) has shown that the electronic angular momentum of the molecular electrons is not very strongly coupled to the nuclear axis.

A molecule of this nature, following Hund's notation,* is said to be of the case (*b*) type. For case (*b*) molecules the quantum numbers involved are J, Λ, S and K, which are, J the total, Λ the projection of the electronic momentum on the nuclear axis, S the electronic spin vector and K the resultant of Λ, and *m*, *m* being the rotational quantum number. For this type the lightly bound electronic spin vector has become completely decoupled and so does not come under consideration.

(*a*) *Electronic Terms.*—The helium band spectrum has been identified with two systems of electronic levels designated ortho- and para- and these are probably triplet and singlet systems, respectively. The para- (or singlet) system is not so well known as the ortho- (or triplet) system owing to the fact that the singlet system is much less intense and so not so fully developed. It is, however, exactly analogous to the triplet system—the same types of electronic terms occurring in each case.†

The electronic terms are divided into three groups according as L the electronic momentum vector is 0, 1 and 2. These three groups are represented by the small letters, *s*, *p* and *d* respectively. They are further associated with different values of Λ, the projection of the electronic momentum vector L on the nuclear axis.‡ The values of Λ are indicated by the capitals Σ, Π and Δ for Λ = 0, 1 and 2 respectively.

It is found that the Σ levels are single and the Π and Δ levels are double. This is explained on Hund's theory as due to the fact that the electrons can rotate equally well in either direction about the nuclei, so giving different orientations of the vector Λ.

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* Hund, 'Z. Physik,' vol. 36, p. 657 (1926); vol. 40, p. 742 (1927) and vol. 42, p. 93 (1927).

† Curtis, 'Proc. Faraday Soc.,' "Molecular Spectra," p. 694 (1929).

‡ Λ is really the resultant of the projections of all the momenta on the nuclear axis.

These general considerations lead to a system of electronic levels such as shown in fig. 3.

The duplication of the levels in the case of $d\Delta$, $d\Pi$ and $p\Pi$ due to the different orientations of the Λ vector is known as " Λ type doubling." The electronic levels produced by Λ type doubling lie fairly close together.

(*b*) *Vibration-rotation Terms.*—For each of the electronic levels indicated above there are corresponding vibration levels with quantum numbers v and rotational levels given by the numbers K (since it is case (*b*) with which we are here concerned).

It is found, however, that the first band $v = 0$ corresponding to $0 \rightarrow 0$ vibrational transition is the most intense, and although other bands have been traced they are very much weaker.

The rotation levels are peculiar in that alternate levels are suppressed. This is due to the fact that the molecule is symmetrical and the nuclei have no spin.

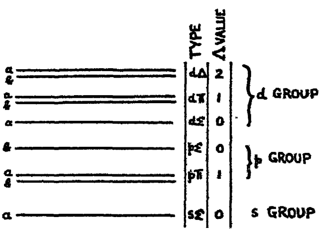

FIG. 3.

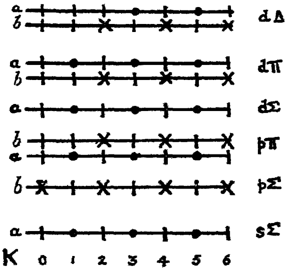

FIG. 4.

In fig. 4 the rotation levels are shown superposed on the electronic levels for the fundamental or $0 \rightarrow 0$ band.

The vertical lines indicate the suppressed levels. The "*b*" levels which exist are shown by crosses, ×, and the "*a*" levels by black dots, • • • •. Observing the condition $\Delta K = \pm 1$ or 0, then the branches are generated by transitions between the × and • levels.

(*c*) *Perturbation Bands.*—In addition to the normal type of band there are bands which show some uncommon structural peculiarities. The rotational levels cannot be represented by parabolic formulæ and in some cases the band is known to have two heads.

These bands known as the "perturbation bands" are produced by the decoupling of the Λ vector from the line of nuclei. Ultimately the Λ vector becomes quantised with respect to the rotational axis. It is the transition from one to the other type of coupling which produces these curious structures.

Bands in the Region λ 6100–λ 6500.

The strong bands in this region (λ 6100–λ 6500) are due to transitions between the levels of quantum number 3 to the lower levels of number 2.

There are three bands of the singlet system, viz. :—

$$3\,{}^1\Sigma \rightarrow 2p\,{}^1\Pi$$
$$3\,{}^1\Pi_a \rightarrow 2p\,{}^1\Pi$$
$$3\,{}^1\Pi_b \rightarrow 2p\,{}^1\Pi$$

each of which shows the perturbations mentioned above and also a band $3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ of the triplet system which is quite normal.

The distribution of the bands can be seen from fig. 2.

Theoretical Intensity Relations in Band Spectra.

From considerations of the quantum theory the intensity of a line emitted from a collection of radiating systems depends in suitable conditions, on the number of emitters N_j present in the higher level E_j of the two levels E_j and $E_{j'}$ concerned in the radiation of a frequency $\nu_{jj'}$ and also upon the probability of spontaneous emission $A_{jj'}$ associated with the two states j and j'.

The total amount of energy (radiation of frequency $\nu_{jj'}$) emitted in all directions per unit time by the radiating systems is

$$N_j\,A_{jj'}\,h\nu_{jj'}, \tag{1}$$

in which N_j depends on the conditions prevailing in the gas (*e.g.*, temperature density of discharge, etc.). $A_{jj'}$ is independent of these conditions and is a characteristic of the gas.

For the case of molecules in an excited state and in thermal equilibrium the population of the two states is governed by the relation.

$$\frac{N_j}{N_{j'}} = \frac{g_j}{g_{j'}} \cdot \frac{\exp\,(-\,E_j/KT)}{\exp\,(-\,E_{j'}/KT)} \tag{2}$$

in which g_j is the statistical weight of the level j.

Equation (1) may now be replaced by

$$A_{jj'}\,h\nu_{jj'}\,g_j\,\exp\,(-\,E_j/KT). \tag{3}$$

The value of E_j is for the *initial* state. Thus the intensity of a given line in a band will be given by

$$I = h\nu_{jj'} A_{jj'} g_j \exp(-E_j/KT). \tag{4}$$

Intensity Factors.

(*a*) *Normal Type.*—The product of the two terms $A_{jj'}\ g_j$ is known as the "intensity factor," i, for the transition $j \rightarrow j'$. The value of g_j is the statistical weight of the level j and is given by $(2j+1)$ so writing $A_{jj'}$ as $A(jj')$, then $A(jj')(2j+1)$ represents the intensity factor.

The values of the $g_j A_{jj'}$ or $(2j+1)A(jj')$ factors have been obtained by London and Hönl (*loc. cit.*), who assumed the usual form of gyroscopic model of the molecule, and more satisfactorily by Rademacher and Reiche,* Kronig and Rabi† and by Dennison‡ using the New Quantum Mechanics.

From an extension of Einstein's§ theory and the correspondence principle we have the relation,

$$A_{jj'}\ h\nu = \frac{(2\pi\nu)^4}{3c^3} \cdot P^2(jj'), \tag{5}$$

where $P(jj')$ is the electric moment corresponding to the particular transition $j \rightarrow j'$.

Equation (5) together with equation (4) gives

$$I \propto \nu^4 g_j P^2(jj') \exp(-E_j/KT). \tag{6}$$

The values of $P^2(jj')$ have been obtained by the authors mentioned above‖ for the normal type of band of case (*a*) molecules. By a simple exchange of quantum numbers as indicated by Mulliken and Kronig¶ the values for case (*b*) molecules may be at once deduced.

The appropriate expressions for a transition such as encountered in λ 6400 (*i.e.*, $3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$) are

$$\Lambda' - \Lambda = 1 \qquad K \rightarrow K+1 \qquad \frac{K+2}{2K+1}, \tag{A}$$

$$K \rightarrow K \qquad 1 \tag{B}$$

$$K \rightarrow K-1 \qquad \frac{K-1}{2K+1}. \tag{C}$$

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* Rademacher and Reiche, 'Z. Physik,' vol. 41, p. 453 (1927).

† Kronig and Rabi, 'Phys. Rev.,' vol. 29, p. 262 (1927).

‡ Dennison, 'Phys. Rev.,' vol. 28, p. 318 (1926).

§ Einstein, 'Phys. Z.,' vol. 18, p. 121 (1917).

‖ Hill and van Vleck, 'Phys. Rev.,' vol. 32, p. 250 (1928).

¶ Kronig, "Band Spectra and Molecular Structure" (Camb. Univ. Press).

Since the quantum weight of the level is (2K + 1) the i factors will be given by (2K + 1) {A ; B ; C}. Thus we have

Branch.	i Factor.	
$K \rightarrow K + 1$	$K + 2$,	(A′)
$K \rightarrow K$	$2K + 1$,	(B′)
$K \rightarrow K - 1$	$K - 1$.	(C′)

Hence the relative intensities of band lines such as those encountered for normal bands of the type $3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ are governed by the three factors ν^4, {A′ ; B′ ; C′} and exp. $(-E_j/KT)$.

(*b*) *Perturbation Bands.*—The theoretical relative intensities in the perturbation bands have been investigated by Kronig and Fujioka* using an elaborate matrix mechanics method.

Fujioka† applied the theory to the perturbation bands of helium, and his data shows close agreement between predicted and experimental values.

It will be seen from fig. 2 that the perturbation bands are much weaker than the normal bands $3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$. The present measurements give the same type of distribution as found by Fujioka. It is probable that for the region of the perturbation bands his measurements are the more accurate and in view of this it was not considered desirable to present a complete treatment of these bands. The results have been included as confirmation of his work.

As mentioned at the outset, we shall direct our attention particularly to the λ 6400 or $3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ band.

Discussion of Results.

Having considered the theoretical type of distribution to be expected in the present case we may proceed to compare the theoretical and experimental values.

(*a*) *The Maxwell-Boltzmann Distribution.*—The complete expression for the intensity of a given band line has been shown above (equation (6)) to be given by

$$I = C\nu^4 i e^{-E/KT}, \tag{7}$$

from which follows

$$\frac{I}{C\nu^4 i} = e^{-E/KT} \tag{8}$$

Equation (8) may now be written

$$\log \frac{I}{C\nu^4 i} = \frac{E}{T} \log e^{-1/K},$$

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* Kronig and Fujioka, 'Z. Physik,' vol. 63, p. 168 (1930).

† *Loc. cit.*

and hence if an exponential type of distribution exists in the tube a plot of log $I/C\nu^4 i$ against E should give a straight line the slope of which is governed by T.

The necessary data for the $3s\,{}^3\Sigma \leftarrow 2p\,{}^3\Pi$ (λ 6400) band is collected in Tables II, (*a*), (*b*) and (*c*).

Table II.

(Data obtained from Table I.)

(*a*) $K \rightarrow K + 1$.

K.	I.	ν.	: ν^4.	$\frac{I}{\nu^4}$	$(K + 2)$ i.	$\frac{I}{\nu^4 i}$	$\log_{10} \frac{I}{\nu^4 i}$	E.
1	82	15595	592	139	3	46·2	1·6646	16
3	125	15565	586	213	5	42·7	1·6304	88
5	130	15534	581	224	7	31·9	1·5038	218
7	123	15503	577	213	9	23·7	1·3747	405
9	94	15472	573	164	11	14·9	1·1732	648
11	64	15441	568	113	13	8·7	0·9395	947
13	38	15410	564	67·4	15	4·5	0·6532	1300
15	24	15378	559	42·9	17	2·5	0·3979	1707
17	14	15346	554	25·3	19	1·3	0·1139	—

(*b*) $K \rightarrow K$ $i = (2K + 1)$.

K.	I.	ν.	: ν^4.	$\frac{I}{\nu^4}$	i.	$\frac{I}{\nu^4 i}$	$\log_{10} \frac{I}{\nu^4 i}$	E.
1	85	15624	596	143	3	47·7	1·6785	16
3	172	15623	596	289	7	41·3	1·6160	88
5	205	15621	596	344	11	31·3	1·4955	218
7	192	15618	596	322	15	21·5	1·3324	405
9	162	15614	593	273	19	14·4	1·1584	648
11	113	15610	593	191	23	8·4	0·9243	947
13	74	15604	592	125	27	4·6	0·6628	1300
15	15(?)	15598	592	25(?)	31	?	?	1707

(*c*) $K \rightarrow K - 1$.

K.	I.	ν.	: ν^4.	$\frac{I}{\nu^4}$	$(K - 1)$ i.	$\frac{I}{\nu^4 i}$	$\log_{10} \frac{I.}{\nu^4 i}$	E.
1	—	—	—	—	—	—	—	16
3	52	15667	603	86·2	2	43·1	1·6347	88
5	79	15694	606	130	4	32·6	1·5132	218
7	80	15721	611	131	6	21·8	1·3389	405
9	(?)	15741	615	—	8	—	—	648
11	(?)	15771	619	—	10	—	—	947
13	34	15794	622	54·7	12	4·55	0·6580	1300
15	22	15816	626	35·1	14	2·51	0·3997	1707
17	14	15836	630	22·2	16	1·38	0·1399	—

The symbols at the head of each column have their usual meaning. The column under E represents the energy corresponding to the initial states and is given in frequency units.* The columns I/ν^4 and I represent relative values of intensity, etc., only, and the absolute values are of no significance. It will be seen from columns 7 and 9 of these tables that the curves resulting from a plot of E against $\log_{10}(I/\nu^4 i)$ will be almost identical. The graph in the case of the P branch is shown in fig. 5.

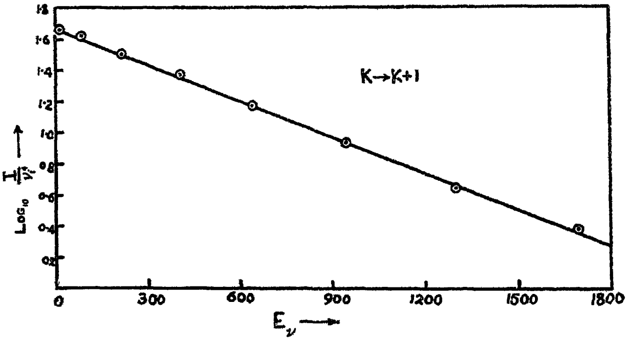

FIG. 5.—Test of Boltzmann Type of Distribution.

From this graph it can at once be seen that a Boltzmann factor is sufficient to explain the observed distribution. All the points lie on a straight line and, further, since from Table II (*a*), (*b*) and (*c*) the three lines for the P, Q and R branches will have identical slopes, the value of T must be common to all three branches.

Using the slope of these lines and observing from equation (9) that

$$\log \frac{I_1/\nu_1^4 i_1}{I_2/\nu_2^4 i_2} = \frac{E_2 - E_1}{T} \log e^{1/K} \qquad (10)$$

or

$$\log (I_1/\nu_1^4 i_1) - \log (I_2/\nu_2^4 i_2) = (E_2 - E_1) \log e^{1/K}/T \qquad (11)$$

and further, if we have E_2 an E_1 in frequency units putting $h = 6\cdot 55 \times 10^{-27}$ erg sec., $k = 1\cdot 371 \times 10^{-16}$ erg/degree, and $c = 3 \times 10^{10}$ cm./sec., then

$$\log \frac{I_1}{\nu_1^4 i_1} - \log \frac{I_2}{\nu_2^4 i_2} = \frac{E_2^{\nu} - E_1^{\nu}}{T} \log e^{\frac{1}{0\cdot 7}}$$

the temperature which must be assigned to the band is 785° K.

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* E given in frequency units is calculated from B the rotational term constant, the K values and frequency data. Mulliken, 'Phys. Rev.,' vol. 29, p. 391 (1927); Kratzer, 'Z. Physik,' vol. 16, p. 353 (1923).

This temperature is higher than the true temperature of the gas molecules (unexcited) of the tube, so it must be regarded as an "effective temperature."

There must be some kind of thermal equilibrium between the emitting molecules, and the fact that the effective temperature is above the temperature of the unexcited molecules may be due to the fact that an emitting molecule is unstable and does not exist long enough to come into equilibrium with the surrounding gas molecules.

Information from other independent sources confirm the view that this effective temperature is the temperature of the emitting molecules.

Measurements of Childs* taken with a Fabry Perot étalon indicate from the width of the band lines that the temperature is of the order 500–1000° K., and further measurements of Langmuir,† using a probe analysis method, support these high temperature values.

There can be no doubt from Tables II (*a*), (*b*) and (*c*) that the three branches have the same "effective temperature," and the conclusion of Childs in connection with the λ 4650 band, that the Q branch owing to the fact that it arises from a different level (see fig. 4) has a different effective temperature, is not substantiated at least in the λ 6400 band, although this corresponds to a similar type of transition ($|\Lambda' - \Lambda| = 1$).

(*b*) *The* i *or Intensity Factors.*—Although the constancy of the corresponding values of $I/\nu^4 i$ in the three tables (*a*), (*b*) and (*c*) of Table II indicates a true assignment of the i values, this may be checked in a more direct way which is independent of any assumptions as to the form of the Boltzmann distribution.

The ratio of the intensities of corresponding lines should be in the ratio of the corresponding i factors, *i.e.*, for the $3s\,{}^3\Sigma \rightarrow 2p\,{}^3\Pi$ band

$$I_P^K : I_Q^K : I_R^K = (K+2) : (2K+1) : (K-1)$$

In making the comparison $I_P^K : I_Q^K : I_R^K$ it is essential that the values I/ν^4 be used rather than I. The writer is not aware that the seriousness of the ν^4 factor has been pointed out before in connection with rotation spectra.

Normally it is assumed that the range of frequencies over which the band is distributed is small, so that the ν^4 factor would be practically constant. Even if this be granted in the case of heavy molecules and the factor there neglected, it is certainly not permissible to do so in this case, *i.e.*, with the light He_2 molecule. Kronig and Fujioka‡ appear to have neglected it in this type of comparison, but, as can be seen for example in the case of $P_{17} : R_{17}$, the effect is in the ratio of 554 : 630, or what amounts to a factor of 12 per cent.

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* *Loc. cit.* 643.

† Langmuir and Mott-Smith, 'Gen. Elec. Rev.,' vol. 27, p. 449 (1924).

‡ *Loc. cit.* 652.

The full curves given in fig. 6 represent the theoretical relation between *i* and K and the corresponding values found experimentally are indicated as points. The agreement is again obvious.

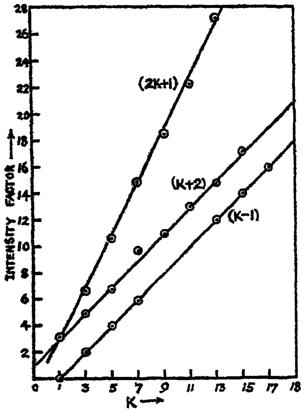

Fig. 6.—Test of Intensity Factors.

(*c*) *The Sum Rule in Band Spectra.*—If the sum rule applies to the present case, viz., that "the sum of the intensity factors

$$A\,(KK')\,(2K+1),$$

for all values of K permitted by the selection rules with K constant is proportional to the quantum weight of the K state," then the relation

$$(I_P^K + I_Q^K + I_R^K) \propto 2K + 1$$

should be satisfied.

In fig. 7 the theoretical and experimental results are compared as before.

The Complete Distribution.

Having shown that the excited molecules may be represented as having an effective temperature corresponding to a thermal equilibrium, and further, that

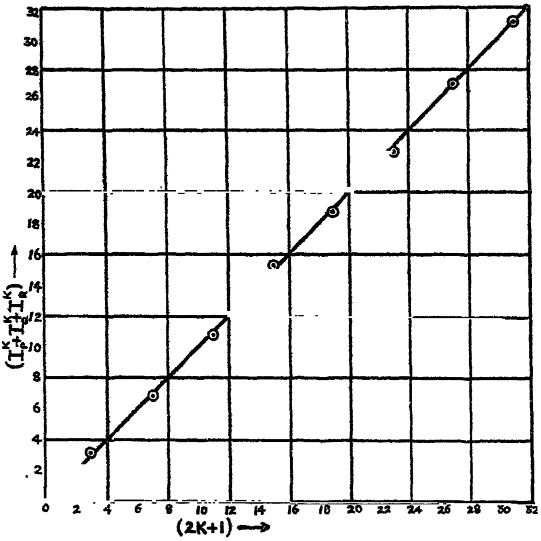

Fig. 7.—Test of Sum Rule.

the experimental *i* values confirm those derived theoretically, the complete theoretical and experimental distribution of intensities may be compared.

In fig. 8 the continuous curve is drawn through the theoretical values of intensity calculated from equation (7) for a temperature T of 785° K. As before, the experimental values are indicated by points.

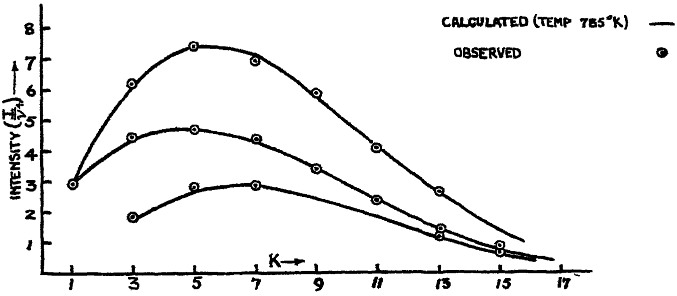

FIG. 8.—Comparison of predicted and observed distributions (temp. 785° K.) for the $3s\,{}^3\Sigma \rightarrow 2p\,{}^3\pi$ helium band.

It will be seen that, except for minor deviations due to the small experimental errors in the measuring of the relative intensities, the experimental values lie very close to the predicted curves.

Conclusion.

These results indicate that in the case of the helium band spectrum for the band λ 6400 an expression of the type of equation (9) is sufficient to represent the relative intensities of the band lines throughout a given band.

Further, since the intensity factors have been established as correct, it follows that the statistical weight of a level K is proportional to (2K + 1) provided the fact is observed that alternate levels (even) are suppressed.

Finally, the results lead inevitably to the conclusion that the assignment of K values must be correct. If it were not so, the agreement between the predicted and experimental intensity values could not possibly exist.

The author wishes to take this opportunity of expressing his thanks to Dr. R. C. Johnson for continuous help and valuable criticism throughout the progress of this work, and to Professor A. Fowler for assistance afforded him at the Royal College of Science while using the recording microphotometer.

Further Investigations with a Wilson Chamber. II.—The Range and Velocity of Recoil Atoms.

By P. M. S. Blackett and D. S. Lees.

(Communicated by Lord Rutherford, F.R.S.—Received October 15, 1931.)

[Plate 11.]

1. *The Range and Velocity of Recoil Atoms.*

In a paper by one of us,* the method of obtaining the relation between the range and velocity of recoil atoms has been described. In the work described in the following paper the same method has been used to extend the earlier results to greater ranges.

Consider a forked track due to an elastic collision between an alpha particle of mass M and initial velocity V and a nucleus of mass m, initially at rest. If ϕ and θ denote the angle of deflection of the alpha particle and the angle of projection of the struck nucleus, and if v_a and v_n are the velocities of the two particles after the collision, we have

$$\frac{m}{\mathrm{M}} = \frac{\sin\phi}{\sin(2\theta + \phi)}, \tag{1}$$

$$\frac{v_n}{\mathrm{V}} = \frac{2\mathrm{M}}{\mathrm{M} + m}\cos\theta, \tag{2}$$

$$\frac{v_n}{v_a} = \frac{\mathrm{M}}{m}\frac{\sin\phi}{\sin\theta}. \tag{3}$$

The lengths R_a and R_n of the tracks of the two particles after the collision are measured and also the distance of the collision from the source; from the last the residual range of the alpha particle can be calculated.

Now the relation between the velocity of an alpha particle and its range, up to about 3 mm. from its end, in any gas mixture can be obtained from Briggs's measurements for air if the variation along the range of the relative stopping power of the gas is known.

Thus the value of v_a can be calculated from the observed value of R_a and so v_n can be calculated from (3), using the observed values of ϕ and θ. Alternatively, V can be calculated from the residual range, and v_n from (2). The value of v_n obtained by either method, together with the observed R_n, gives one point on the curve connecting the range and the velocity of the recoil atom.

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* Blackett, 'Proc. Roy. Soc.,' A, vol. 103, p. 62 (1923).

In the paper describing the use of this method (*loc. cit.*) range velocity curves for hydrogen, air and argon recoil atoms were determined up to air equivalent ranges of 1·0, 2·5 and 0·8 mm. respectively. In this paper the determinations have been made much more precise and have been extended up to ranges of 10, 6 and 3 mm. In addition, an accurate determination of the velocity of alpha particles themselves over the last 2·5 mm. of their range has been made. The data available from the study of nitrogen disintegration photographs, concerning the range of O_{17} atoms, is also given.

Some 1,300,000 tracks were available for this work, made up as follows*:—

A. 750,000 in 50 per cent. argon, 10 per cent. oxygen, 40 per cent. hydrogen.
B. 350,000 in 50 per cent. nitrogen, 10 per cent. oxygen, 40 per cent. hydrogen.
C. 40,000 in 75 per cent. hydrogen, 25 per cent. oxygen.
D. 60,000 in 50 per cent. methane, 50 per cent. hydrogen.
E. 100,000 in 75 per cent. helium, 25 per cent. oxygen.

All the photographs were taken with a special camera and an automatic Wilson chamber designed by one of us.†

Of the two ways of obtaining v_n the first is always to be preferred, when it is possible, that is, when the alpha particle stops in the chamber, so that R_α can be measured. For, in the second method, errors in V will arise if all the alpha particles leaving the source have not very nearly the same velocity, and when the source is not clean this always happens. The second method is used where necessary for collisions that occur near the source, but not, when it can be avoided, for collisions near the end of the range, since in these the residual range would be inaccurate as it would be given as the difference of two much larger lengths. Using either method, if the value of m/M for any collision is assumed known, two independent determinations of v_n can be made, since ϕ and θ are related by (1). For v_n can be calculated from (3), using the measured value of ϕ and the value of θ calculated from (1); or, alternatively, using the measured value of θ and the calculated value of ϕ. The precision of these two determinations may be very different. To illustrate this, consider the collision between an alpha particle and a hydrogen nucleus. Then from (1) a point representing the true angles ϕ and θ must lie on the curve

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* The films E were taken by Mr. Champion and one of us (P.M.S.B.) in 1930. The others by D.S.L. in 1926–29.

† Blackett, 'Proc. Roy. Soc.,' vol. 123, p. 613 (1929); 'J. of Sci. Inst.,' vol. 6, p. 184 (1929).

$$\sin\phi/\sin(2\theta+\phi) = 0\cdot252.$$

Let the curve, fig 1, represent this relation. Owing to the unknown observational errors $\delta\phi$, $\delta\theta$, the point corresponding to the measured values of ϕ and θ will lie off the curve, say at P. If now the probable errors $\delta\phi$, $\delta\theta$ are taken as equal, then the most probable values of ϕ and θ are those corresponding to the foot P_0 of the perpendicular from P on to the curve, since the choice of this point makes the sum of the squares of the errors a minimum.

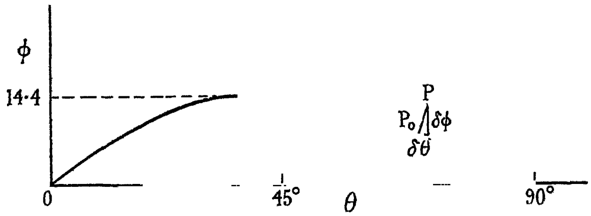

Fig. 1.

When the probable errors in ϕ and θ are not the same, the graphical method can still be used provided the scales of ϕ and θ are altered in the inverse ratio of their probable errors; or, alternatively, by using a suitably weighted mean of the two independent determinations.

An extreme, but important, case of this procedure is furnished by any hydrogen collision for which θ has a value about 40°. From* fig. 1, it is seen that ϕ then has its maximum value of 14·4°. Suppose now that $\phi_{\text{obs.}} = 15\cdot4°$, then the error in v_n as calculated from $\phi_{\text{obs.}}$, will be 7 per cent. But since we have assumed $\theta_{\text{obs.}}$ to be about 40°, it is almost certain that the true value of ϕ is 14·4. If we assume this value, the error in v_n now only depends on that in θ, and, if this again is 1°, the resulting error in v_n is only 2 per cent., instead of 7 per cent.

2. It is explained in the third paper how the measured lengths of the images are converted into *reduced air ranges*. The method is to measure the length L_0 of the image on the film of a full-length alpha ray track of range R_0 in air at 15° C., 760 mm.† and to multiply the measured length L_α of the image

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* See also fig. 1 of Paper I.

† In this work R_0 is always 4·8 or 3·9 cm. corresponding to the alpha-particles from ThC or polonium.

of any part of the track by R_0/L_0, so that its reduced air range R_a is given by

$$R_a/L_a = R_0/L_0. \tag{4}$$

The reduced air range of any part of a track in any gas mixture is therefore the range the part of the track would have in air at N.T.P. if the stopping power of the mixture relative to air was constant along the range. When this is not so, it is necessary to calculate the *air equivalent range* R_a' from the *reduced air range* R_a. The former is the distance the particle would actually travel in air at N.T.P. This can be done, following Gibson and Gardiner,* if it is known how the stopping power relative to air of the gas mixture varies along the range.

Let $\sigma(x)$ denote the differential stopping power of the mixture for alpha particles of residual range x in air.

Then the actual range in the gas mixture at N.T.P. of an alpha particle with an air equivalent range R_a' is

$$\int_0^{R_a'} \frac{dx}{\sigma(x)} \ldots,$$

and the actual length of the photographic image is

$$L_a = K \int_0^{R_a'} \frac{dx}{\sigma(x)} \ldots,$$

where K is a factor due to the magnification, expansion ratio and initial pressure and temperature. Then from (4)

$$R_a = \frac{R_0}{L_0} L_a = R_0 \frac{\int_0^{R_a'} \frac{dx}{\sigma(x)}}{\int_0^{R_0} \frac{dx}{\sigma(x)}}. \tag{5}$$

If $\sigma(x)$ does not vary with x, $R_a = R_a'$, so that the air equivalent range equals the reduced range. When $\sigma(x)$ varies with x, they are different, except at the limits $R_a = R_a' = 0$ and $R_a = R_a' = R_0$. Since the difference between R_a' and R_a is never very large it is the variation of σ with x which is required rather than its absolute value; it is not, therefore, necessary to know the exact composition of the gas. Nor is it required to know the magnification of the camera or the expansion ratio at the instant of track formation, or the initial pressure and temperature.

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* Gibson and Gardiner, 'Phys. Rev.,' vol. 30, p. 541 (1927); see also Harper and Salaman, 'Proc. Roy. Soc.,' A, vol. 127, p. 175 (1930).

3. *The Range Velocity Curve for Slow Alpha Particles.*

The accurate measurements of Briggs* by the magnetic deflection method give the velocity of alpha particles in air down to 3 mm. from the end of their range. By photographing tracks in a gaseous mixture containing helium,† collisions between alpha particles and helium nuclei can be obtained, and these enable the range velocity curve to be extended to within a fraction of a millimetre of the end of the range. Since from Gurney's‡ measurements the stopping power of helium only increases from 0·175 to 0·179 as the range is decreased from 3·9 cm. to zero, while that of oxygen decreases from 1·05 to 0·98, the variation of σ with x for this mixture will be neglected, and the air equivalent range can be taken as equal to the reduced air range. Consequently for any track for which $R_\alpha > 3$ mm. the velocity v_α can be taken directly from Briggs's results.

The results for 38 tracks are shown in fig. 2, each point representing a velocity determination from a single collision. The full curve, drawn smoothly through the points, agrees very closely with the curve obtained by extrapolating Briggs's results, and is slightly below the rough curve originally obtained by Blackett§ from a statistical analysis of the collisions of slow alpha particles. The velocities obtained from this curve were used by Blackett and Champion‖ when verifying Mott's theory¶ of the scattering of slow alpha particles by helium. The very good agreement there obtained between the observed and calculated scattering gives a valuable independent check on the accuracy of these values, since the scattering depends on the fourth power of the velocity.

The final values for the velocity of an alpha particle in air near the end of its range are given in Table I. The values for 0·5, 1·0, 2·0 mm. range are derived from the present investigation, the others from Briggs's results.

For comparison with experiments with helium positive rays the voltage necessary to accelerate a *singly* charged helium ion to the corresponding

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* Briggs, 'Proc. Roy. Soc.,' A, vol. 114, p. 341 (1927).

† The actual mixture was about 75 per cent. helium and 25 per cent. oxygen. A polonium source was used.

‡ Gurney, 'Proc. Roy. Soc.,' A, vol. 107, p. 341 (1925). See also Gibson and Gardiner, (*loc. cit.*), and Gibson and Eyring, 'Phys. Rev.,' vol. 30, p. 583 (1927), and Salaman and Harper, 'Proc. Roy. Soc.,' A, vol. 127, p. 175 (1930).

§ Blackett, 'Proc. Roy. Soc.,' A, vol. 102, p. 294 (1922).

‖ Blackett and Champion, 'Proc. Roy. Soc.,' A, vol. 130, p. 380 (1931).

¶ Mott, 'Proc. Roy. Soc.,' A, vol. 126, p. 259 (1930).

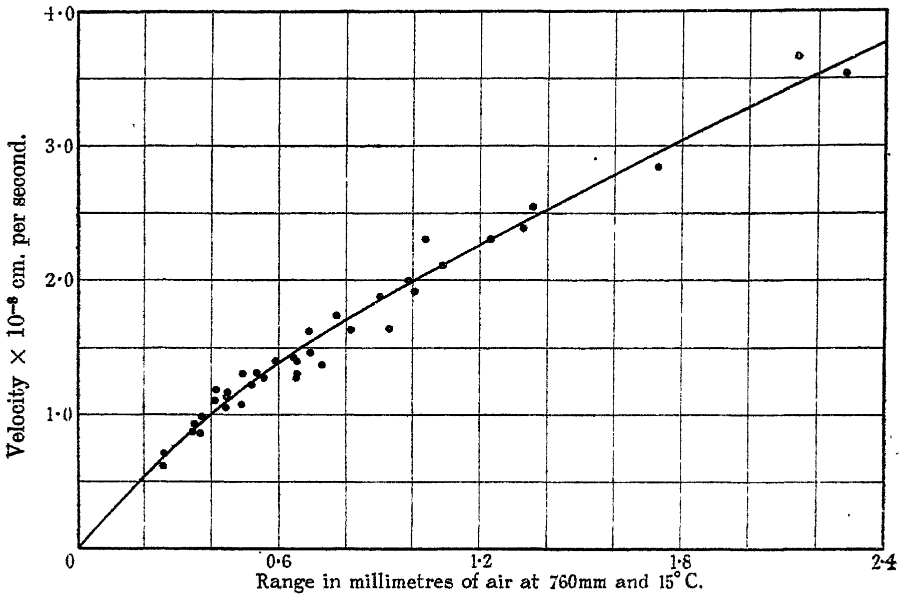

FIG. 2.—Velocity of α particles in the last 2·4 millimetres of their range in air.

Table I.—Range and Velocity of Slow Alpha Particles.

Range in air at 760 mm. 15° C., mm.	0·5	1·0	2·0	3·0	4·0	6·0	8·0	10·0
Velocity of alpha particle, cm. per sec. × 10^{-8}	1·22	2·00	3·30	4·27	5·35	6·94	8·21	9·25
Energy of He^+ ion in volts × 10^{-3}	30·8	83·0	226	392	594	988	1390	1770
Velocity calculated from $R = 0{\cdot}372\,V^{1{\cdot}43}$	1·23	2·00	3·24	4·30	5·25	7·00	8·53	9·98
Percentage error	+1	0	−2	+1	−2	+1	+4	+7

velocity is also given. Between the ranges 0 to 6·0 mm. the velocity obeys the relation

$$R = 0{\cdot}372\,V^{1{\cdot}43}$$

within a maximum error of 2. per cent. The values calculated from this expression and the percentage errors are also given.

The distance from the end of the range at which the rate of loss of energy is a maximum, can be found from the observed relation between velocity and range. For alpha particles in air, this maximum energy loss is found to occur about 6·0 mm. from the end of the range. This result, which depends only on Briggs's measurements, and not on the present investigation, is somewhat higher than the result of the measurements of I. Curie* and Nimmo and

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* Curie, 'Ann. Physique,' vol. 3, p. 799 (1925).

Feather,* who found 4·5 and 3·0 mm. respectively, for the position of the maximum ionisation. It is possible that the maximum of energy loss and the maximum ionisation occur at different velocities. This would correspond to a changing value of the energy lost for one ion. But it is also possible that Briggs's results may be slightly in error. This is supported by the fact that the measured range of the alpha particles from polonium is about 0·5 mm. less than that to be expected from Briggs's results. If such an error exists at 3·9 cm. range, the error at 4 to 10 mm. may be great enough to cause this discrepancy. In consequence of this, the relation given above is possibly not valid beyond about 4 mm. range.

4. *The Range Velocity Curve for Slow H-particles.*

All the photographs mentioned in Section 1 except E were obtained with a gas mixture containing hydrogen, so a large number of forks due to the collisions of alpha particles with hydrogen nuclei were available. Since the stopping power of hydrogen relative to air varies very considerably along the range, it is necessary to apply the method of Section 2 in order to be able to calculate the velocity of an alpha particle of given residual range, in the gas. The actual amount of the correction is not very large, as the hydrogen was mixed with other gases. Gurney (*loc. cit.*) gives the values 0·214, 0·247, 0·309 for the stopping power of hydrogen relative to air for the following range limits, 3·8 to 3·5 cm., 1·4 to 0 cm., 0·35 to 0 cm. From these figures we can obtain the following *approximate* values† for the differential stopping power along the range. The values are chosen so as to give the measured average values correctly.

The mean value of σ over the last 4·8 cm. is 0·224. The last row gives the estimated differential stopping power of H-particles in H_2 (see p. 666).

Using these values for hydrogen and the values for O_2, N_2 and A from Gurney's measurements, we are enabled by rough numerical integration of (5) to obtain

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* Nimmo and Feather, 'Proc. Camb. Phil. Soc.,' vol. 24, p. 139 (1928).

† Gibson and Gardiner and Gibson and Eyring (*loc. cit.*) have derived the differential stopping power of hydrogen from their measurements of the average stopping power. They find that σ falls again at the end of the range. This result seems somewhat doubtful, as the measured values for 3·5 to 0 mm. must, owing to the inhomogeneity of the beam, actually refer to particles of mean range of perhaps 1 mm. This hypothetical fall at the end has been neglected here, but would not make very much difference if it had been taken into account.

Table II.—Approximate Differential Stopping Power of Hydrogen for Alpha Particles and H-Particles.

Range in cm. air	0	0·1	0·3	0·5	1·0	2·0	4·0
σ alpha-particles	0·34	0·31	0·26	0·24	0·220	0·217	0·214
σ H-particles	0·42	0·33	0·27	0·24	0·220	0·217	0·214

R_α' from R_α and so to construct the curve connecting the velocity with the reduced range in the mixture.[*]

In fig. 3 are shown the results of the measurement of 69 hydrogen forks

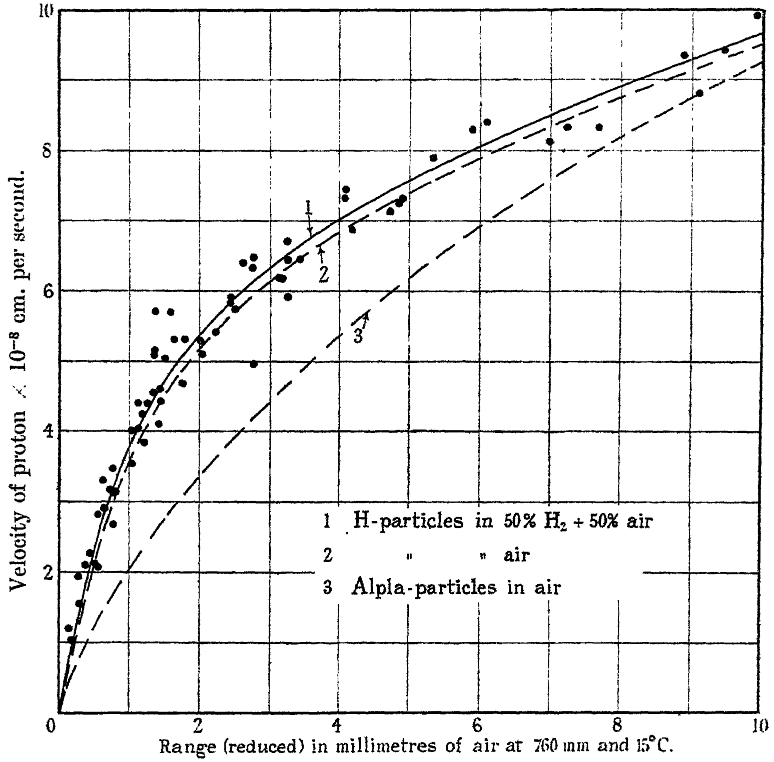

Fig. 3.—Range and velocity of H-particles.

[*] It is convenient to give here the velocity of an alpha-particle along the last part of its range in pure hydrogen, as determined by this method, since this will be required for the theoretical discussion in a subsequent paper. In addition is given the range of H-particles in hydrogen, obtained from the curve for air using the data of Table II.

Range of Slow Alpha Particles and H-particles in Hydrogen.

Velocity, cm. per sec. × 10^{-8}	2	4	6	8	10
Range of alpha-particles in H_2, mm.	3·2	8·9	17·3	29·0	46·4
Range of H-particles in H_2, mm.	1·0	3·5	8·8	21·6	(44·4?)

taken from the million or so tracks on the films A, B, C and D. All the available forks for which the length R_H of the H-particle had a length of some millimetres were utilised, but, of course, only a small fraction of the large available number of very short forks.* The spread of the dots representing the measurements of individual tracks is probably mainly due to the errors of measurement of the angle of deflection ϕ of the alpha particle. The average value of ϕ for the tracks was about 10°, and, as in Paper 3, it is concluded that the average error of angle measurement for such tracks is about $\frac{1}{2}°$, it is to be expected, in view of (3), that the dots will have an average deviation from the mean curve of about 5 per cent. The actual spread is of just about this amount. The probable error of the determination of the ordinates of the curve is estimated as about 2 per cent., except for the higher ranges where it is greater owing to the scarcity of the data.

The mean curve drawn through the points, curve 1 in fig. 3, gives the velocity of an H-particle against the reduced range in the mixture. To obtain the form of the curve for H-particle in air, the method of Section 2 can be applied again, if the variation of stopping power of the mixture for H-particles is known. Now the stopping power of a gas for fast H-particles is the same as for fast alpha particles. The only relevant measurements of the stopping power for slow H-particles are those of Gerthsen,† who finds that the stopping power of hydrogen relative to air is 0·40 for H-particles of range about 0·7 mm. of air. As this is not very much greater than the value for alpha particles, obtained by extrapolating the figures of Table II, one is able to construct a reasonable rough curve for the stopping powers of hydrogen for H-particles. These have been given in Table II. By using equation (5) in the same way as before we obtain curve 2 in fig. 3. This gives the velocity of an H-particle along the last 10 mm. of its range in air. As the total correction for varying stopping power is never here more than 5 per cent., the uncertainties in the stopping powers are of little account, since the accuracy of the velocity determination is not much better than 2 per cent.

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* In addition to the data given in the diagram, three tracks were obtained in which R_H was greater than 10 mm. of air. The results of the measurements were as follows :—

Range in millimetres air	15·90	34·2	35·0
Velocity of H-particle cm. per sec. × 10^{-8}.........	11·9	14·7	14·8
Velocity of alpha-particle of same range, cm. per sec. × 10^{-8}	11·4	15·1	15·2

The figures in the last two rows agree within the experimental error. The accuracy is not sufficient to detect the slight difference to be expected (Blackett, *in the press*).

† Gerthsen, 'Ann. Physik,' vol. 5, p. 657 (1930).

The curious concentration of high points between ranges of 1 and 2 mm. may well be due to chance, but may indicate some anomalous energy loss.

In Table III these results are given in tabular form, together with the voltage required to accelerate an H-particle to the given velocity.

Table III.

Range of H-particle in air, 15° C., mm.	0·5	1·0	2·0	3·0	4·0	6·0	8·0	10·0
Velocity $\times 10^{-8}$ cm. per sec.	2·11	3·53	5·13	6·11	6·86	7·99 (8·1)	8·82 (9·1)	9·55 (10·0)
Energy in volts $\times 10^{-3}$	23·2	65·2	137	195	246	340 (350)	406 (432)	476 (522)

It is shown in another paper* that there are certain theoretical reasons to believe that the measured velocities for the larger ranges are too low. The figures in brackets are those suggested by the theoretical argument. The differences are not much greater than the experimental error.

The relation between v and R cannot usefully be expressed in the form $R \alpha v^n$, since n varies from 1·2 at low ranges to 3·0 at 10 mm. The distance from the end of the range of an H-particle in air at which the energy loss is a maximum is found to be about 1 mm., the corresponding velocity is therefore about $3 \cdot 3 \times 10^8$ cm. per second.

In fig. 4 the full line repeats these results for the last 1·5 mm. of the range on a larger scale. The values obtained by one of us† by the same method are also shown. The exact agreement is fortuitous as the earlier measurements were only rough. Gerthsen (*loc. cit.*) has recently determined the range of H-particles of energies between 27,000 and 57,000 volts by positive ray method. His results should be the more exact, as the precision of our measurements of the small lengths and angles in this region is not very great. The agreement between the two methods is very satisfactory. Finally, there is also shown the result of a rough statistical analysis of the collisions of the H-particles themselves with oxygen atoms. The method is essentially that described previously by one of us. Some 160 hydrogen spurs were observed and the number of collisions with oxygen atoms of given angle and residual range were counted. The results were as follows. Between ranges 0·22 and 0·40 mm. 17 collisions over 20° were found. Between 0·40 and 0·65 mm. 11 collisions over 10° were found. By using the classical scattering formulæ the velocities at the mean ranges of 0·30 and 0·52 mm. are found to be 1·50 and $2 \cdot 55 \times 10^8$ cm.

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* Blackett, 'Proc. Roy. Soc.' (*in the press*).

† Blackett (1922), *loc. cit.*

per second. Considering the scarcity of the data and the difficulty of the measurements, this determination gives a useful and completely independent check on the order of magnitude of the velocities and also gives a test, even if only a rough one, of the validity of the classical scattering laws for collision of slow H-particles and oxygen nuclei.

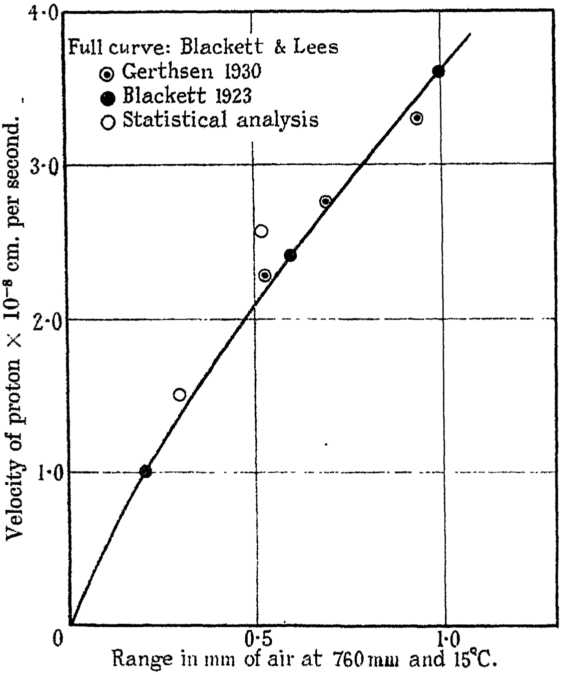

FIG. 4.—Range and velocity of H-particles near end of range.

The lowest curve (3) on fig. 3 gives the velocity of an alpha particle for comparison with velocity of an H-particle of the same range. The difference between these two curves is of considerable theoretical interest and will be discussed later.

5. *The Range Velocity Curves for Nitrogen, Oxygen* (O_{16} *and* O_{17}) *and Argon.*

The accuracy of the measurements of lengths and angles is not sufficient to enable a collision with an oxygen atom to be distinguished from one with nitrogen, but either can be distinguished from a collision with argon by the length of the spur. The 750,000 tracks in 50 per cent. A, 10 per cent. O_2, 40 per cent. H_2 provide data for the range velocity curves for oxygen and argon. The 350,000 tracks in 50 per cent. N_2, 10 per cent. O_2, 40 per cent. H_2, give the data for nitrogen. A small correction is applied for the probable fraction of the collisions which were with oxygen.

The results for argon are given in fig. 5, and those for oxygen and nitrogen in fig. 6. In Table IV are tabulated the velocities of oxygen and nitrogen atoms along the last 6 mm. of their range. It will be seen that the ratio of the range of an O_{16} atom to that of an N_{14} atom of the same velocity is 1·09. This is in good agreement with the value 1·07 obtained by assuming a relation* of the form

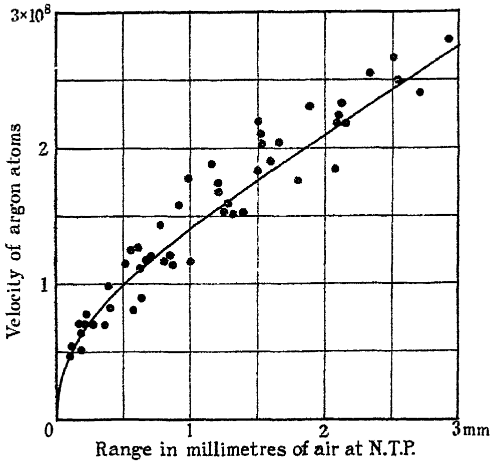

Fig. 5.—Range and velocity of Argon Recoil Atoms.

$$R \propto mz^{-\frac{1}{2}} f(v) \qquad (6)$$

where z is the atomic number of the particle. But as neither determination is very exact, the probable error being about 3 per cent., no great weight can be placed on the exact value of the ratio found.

The range of atoms of O_{17} can be obtained from measurements of nitrogen disintegration photographs (Blackett, *loc. cit.*), that is, of those collisions of alpha particles with nitrogen nuclei in which a proton is ejected and the alpha

Table IV.—Range and Velocity of Nitrogen and Oxygen Atoms.

Velocity, cm. per sec. × 10^{-8}	1	2	3	4	5	6	7
Range in air of *nitrogen*	0·50	1·28	2·10	2·92	3·72	4·54	5·35
Range in air of *oxygen* (O_{16})	—	1·40	2·30	3·17	4·07	4·94	5·80

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* Blackett, 'Proc. Roy. Soc.,' A, vol. 107, p. 349 (1925).

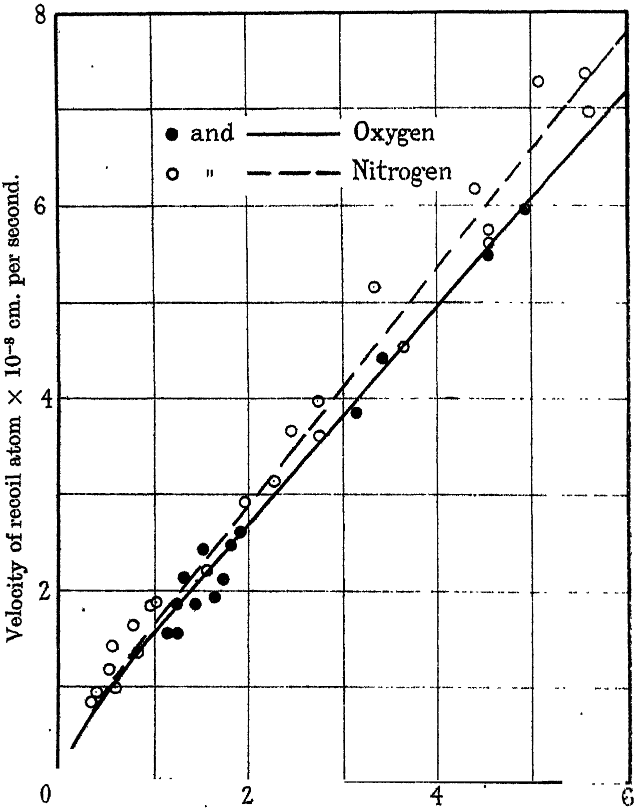

Fig. 6.—Range and velocity of Nitrogen and Oxygen Recoil Atoms in Air.

particle is captured. Of the 13 tracks available,* 7 are suitable for the range velocity determination. In Table V are given the measured ranges of the O_{17} atom together with the ranges, taken from fig. 6, of an N_{14} atom of the same velocity. The mean of the ratio of the two is 1·15, while the expression (6) gives a value of 1·14.

Table V.—Comparison of Range of O_{17} and N_{14} Atoms.

Range of O_{17} atom, mm. air	2·25	2·52	2·78	2·94	3·00	3·42	4·30
Range of N_{14} atom, mm. air	2·00	2·07	2·55	2·52	2·60	2·80	4·00
Ratio	1·13	1·22	1·09	1·17	1·15	1·21	1·07

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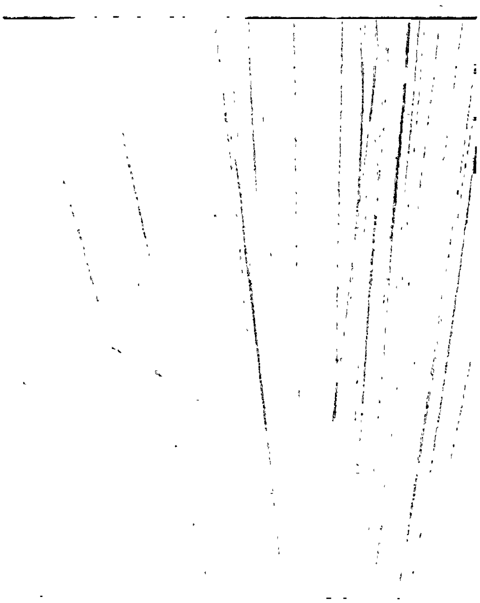
* Including one obtained by Harkins, 'Phys. Rev.,' vol. 35, p. 809 (1930).



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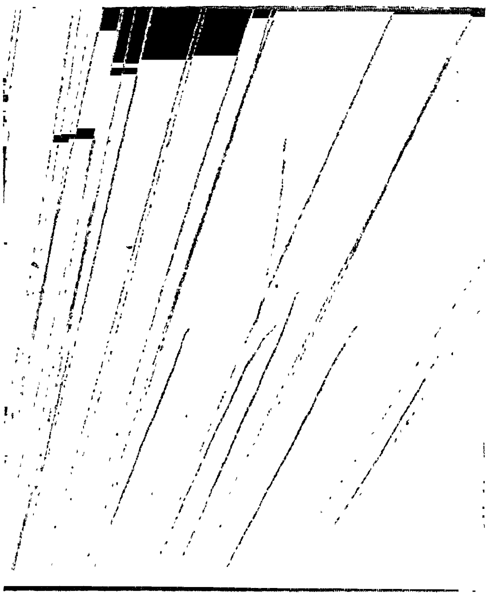

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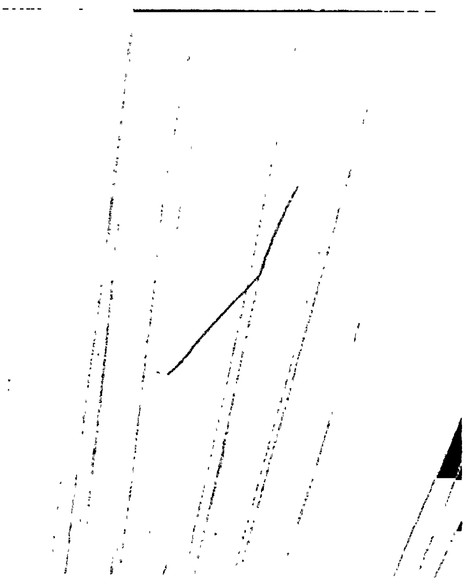

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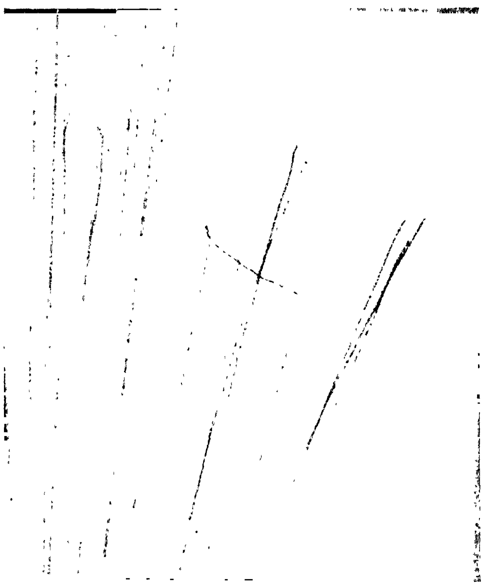

4.

(*Facing p.* 671.)

Summary.

The Wilson cloud method is applied to determine the relation between the velocity and range of H-particles, alpha particles, nitrogen, oxygen (O_{16} and O_{17}) and argon atoms. The method is that previously used by Blackett, but the large number of new photographs available allow the results to be extended to greater ranges and velocities.

We are indebted to Mr. J. S. Barnshaw, of King's College, for assistance with the numerical calculations, and to King's College for a grant from the Research Fund.

One of us (D.S.L.) is indebted to the Department of Scientific and Industrial Research for a grant during the years 1926–29, during which the experimental work was carried out. Part of the cost of the work has been borne by a grant for apparatus from the same Department.

DESCRIPTION OF PLATE.

	ϕ °	R_α mm.	R_H mm.
FIG. 1.—Elastic collision with hydrogen ………	11·2	18·2	15·9
FIG. 2.—Elastic collision with hydrogen ………	7·0	2·2	12·5
FIG. 3.—Elastic collision with nitrogen …………	141·9	6·60	4·55
FIG. 4.—Elastic collision with argon ……………	115	6·4	0·8

In fig. 2 it will be noticed that the H-particle travels nearly six times as far as the alpha particle.

The Distribution of Energy in the β-Ray Spectrum of Radium E.

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(Communicated by Lord Rutherford, F.R.S.—Received October 15, 1931.)

[PLATE 12.]

1. *Introduction.*

There exists some conflicting experimental data concerning the distribution of energy in the β-ray spectrum of radium E. The earliest work, carried out by Schmidt* in 1907, using both the absorption and magnetic deflection methods, showed that the spectrum was apparently continuous but had a well-marked upper limit at about Hρ 5500 (energy about 10^6 volts). In 1911, O. v. Baeyer, Hahn and Meitner† confirmed this result and Gray‡ came to a similar conclusion in the following year. Danysz,§ however, using the method of magnetic focussing, while agreeing to the main distribution including the existence of the well-marked upper limit at 5500 Hρ, made a guarded statement concerning the possibility of the existence of β-rays of far higher velocities. " Sur ces mêmes clichés, il semble y avoir des indices d'un faisceau beaucoup plus rapide, de vitesse variable comme le premier (comprise entre les limites approximatives $\beta = 0 \cdot 94$–$0 \cdot 99$). Toutefois ces indices sont tellement faibles qu'il est nécessaire de recourir à une autre methode pour être sûr de son existence. Ce faisceau est beaucoup moins visible que le faisceau le plus rapide du radium C . . ." In 1916, Kovarik and McKeehan,|| using the ionisation method, considered their results agreed with those of O. v. Baeyer, Hahn and Meitner. Curie and D'Espine,¶ in 1925, using the method of direct magnetic deviation and a photographic plate, agreed to the sharp upper limit of the main distribution, but found also a very weak band between the limits of 7000–10,000 Hρ (energy $1 \cdot 5 \times 10^6 - 3 \cdot 0 \times 10^6$ volts). It appears that there was no evidence of any direct connection between the two parts of the spectrum. The subject was considered again in 1927 by Yovanovitch and D'Espine** and

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* 'Phys. Z.,' vol. 8, p. 361 (1907).

† 'Phys. Z.,' vol. 12, p. 273 (1911).

‡ 'Proc. Roy. Soc.,' A, vol. 87, p. 487 (1912).

§ 'Ann. Chim. (Phys.),' vol. 30, p. 241 (1913).

|| 'Phys. Rev.,' vol. 8, p. 574 (1916).

¶ 'C. R. Acad. Sci.,' vol. 181, p. 31 (1925).

** 'J. Physique,' vol. 8, p. 276 (1927).

the previous results of the latter were confirmed. The same year, Madgwick,* using the ionisation method, confirmed the existence of a sharp upper limit at 5000 Hρ and stated "there is no reason to doubt the accuracy of the endpoint." In a short letter to 'Nature' in 1929, Gray and O'Leary† mention an experiment, using the magnetic deflection and ionisation method, and conclude that less than one particle in 25,000 is emitted with Hρ greater than 8000.

Recently, however, F. R. Terroux,‡ using an expansion chamber, finds no indication of the sharp upper limit of the main spectrum at Hρ 5000, but a gradual tailing off to very high velocities in a manner which, he suggests, indicates a Maxwellian distribution. This would be a point of fundamental importance in attempting any theory of the primary disintegration process, for although it does not give any picture of the nucleus before emission, it imposes a strict criterion which any proposed mechanism must satisfy. In particular, he estimates the number of particles with Hρ greater than 5000 to be as high as 4 per cent. of the total number of particles emitted. This result is in direct contradiction to all previous work and it is clearly important to repeat the investigation using the same method. The advantages of the expansion chamber method are well known; in the problem in hand, the almost equal sensitivity to particles of all velocities is the point of greatest importance. The writer has recently obtained a large number of photographs of β-ray tracks in an automatic expansion chamber. The source was an old radon bulb and the experimental disposition such as to render the results suitable for the investigation of the upper half of the β-ray spectrum of radium E. The existence of the sharp upper limit at about 5000 Hρ has been fully confirmed. No evidence of any gradual tailing off was found and it is estimated that less than one particle in 2000 is emitted with Hρ greater than 5500.

2. *Experimental Method.*

The automatic expansion chamber used was a modification of that previously employed by Blackett and the writer§ for the production of α-ray photographs; it uses the disposition of two cameras mutually at right angles. The main alterations are summarised in what follows; briefly, it may be stated that the improvements in technique have consisted largely of refinements of the critical adjustments. Fast β-ray tracks are always difficult to photograph owing to the very small limits between which the expansion ratio can be varied for the production of fine clear tracks and to the very small amount of light scattered by the few individual drops per centimetre of the fast β-ray track. These difficulties become very great indeed when a large number of fast β-ray photographs is required in a reasonably short time. The expansion chamber was of the standard pattern, being about 16 cm. in diameter and about 6 cm. deep; a small window in the cylindrical wall was about ½ cm. in diameter and was covered with a thin piece of aluminium foil, equal in stopping power for α-particles to about 4 cm. of air. The shutter was a simple brass bar arrangement with a lead strip attached to one end. It was actuated by a spring and released by a Bowden wire attached to the main driving mechanism, as already described by Blackett.* The source was an old radon bulb and was placed behind a lead slit, 5 mm. broad, 10 mm. long, and 0·5 mm. high. This served to define a flat beam of rays in the plane of the chamber. The source itself was placed in a small brass holder which was open at the end facing the chamber, thus producing very few scattered particles in the forward direction. The holder slid to and from the chamber window on a steel rod, thus rendering it possible to adjust easily the number of tracks per photograph. The whole source and slit arrangement rotated about a brass support, so that the entering beam of rays could be inclined at any mean angle to the window.

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* 'Proc. Camb. Phil. Soc.,' vol. 23, p. 970 (1927).

† 'Nature,' vol. 123, p. 568 (1929).

‡ 'Proc. Roy. Soc.,' A, vol. 131, p. 90 (1931).

§ 'Proc. Roy. Soc.,' A, vol. 130, p. 380 (1931).

The rate of taking photographs was about one per minute and one intermediate expansion was found quite sufficient to clear the field from the old tracks of the previous expansion. Any attempt to increase the speed of taking photographs was unsuccessful, as a chamber of the above dimensions does not reach thermal equilibrium in less than 1 minute. The expansion ratio is then no longer constant and successive photographs show marked differences in appearance. The writer found that the diatomic gases (nitrogen and oxygen) functioned best when the expansion ratio was just under 1·31, the actual method of procedure being to raise the expansion ratio to that value and then to make the final adjustments, using the visibility of the tracks as a guide. At a certain critical value, the tracks take on a particularly fine beady appearance which is strikingly different from their appearance when the expansion ratio is even 0·005 away from this critical value. The nature of the gas in the chamber, of course, strongly affects the appearance of the tracks. Oxygen gives fine tracks over a comparatively wide range of expansion ratio, but in nitrogen, unless special precaution is taken over this factor and the timing of the shutter, the tracks tend to be diffuse. Although early experiments were made in oxygen, all the tracks analysed here were taken in nitrogen. The reason for this was the persistent appearance of general cloud in the chamber when the former gas was used. This contamination is no doubt due to the formation of chemical condensation nuclei, owing to the high chemical activity of the oxygen.* The result is, that about half-an-hour after the apparatus has been working, the tracks commence to be formed against a considerable and continually increasing background of drops; to reduce this background it is necessary to lower the expansion ratio with a consequent increase of diffuseness in the appearance of the tracks. With nitrogen in the chamber, the trouble was very much less in evidence and this gas was therefore used throughout the present experiment. The nitrogen was changed once a day.

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* 'Proc. Roy. Soc.,' A, vol. 123, p. 613 (1929); 'J. Sci. Inst.,' vol. 4, p. 433 (1927); etc.

For illuminating the tracks, the usual method of a powerful electrical discharge through two mercury vapour lamps, was used; the capacity of the condenser supplying the two lamps was about one-tenth of a microfarad, the voltage about 40,000, and the internal diameter of the quartz capillary about 3 mm. It was necessary to employ oblique illumination to obtain adequate intensity of the photographic image. The illuminating beam was inclined at about 30° to the axes of the cameras and therefore at about 15° to the horizontal plane of the chamber. With such an experimental disposition and a chamber of the dimensions used here, the beam of light illuminated the peripheral parts of the glass roof of the chamber. Careful screening was therefore necessary and a circular annular black screen of about 12 cm. internal diameter was fixed to the roof of the chamber (see fig. 1).

The magnetic field which was used for determining the velocities of the β-particles was supplied by a pair of Helmholtz coils with their common axis perpendicular to the plane of the chamber. The field was tested over the area and depth occupied by the illuminated tracks and found to be constant to ½ per cent. A field of about 250 gauss was used in this experiment; it was measured independently with a fluxmeter and a ballistic galvanometer. The method of analysis of the tracks utilises two cameras at right angles; consequently, the circles into which the β-ray tracks are bent by the applied field project into ellipses on the photograph. The measurement of these ellipses and their computation back into circles is laborious; a series of about 120 artificial tracks of known curvature (drawn on white paper in Indian ink) were therefore photographed in the position of the natural tracks and the resulting ellipses, corresponding to circles of known radius of curvature, simply slipped over the photographs of the natural tracks, until a fit was obtained.

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* In particular, the growth of bacteria in the gelatin used for sealing part of the chamber and for covering the floor, is a disturbing factor. In growing, the bacteria liberate carbon dioxide, alcohols and other fermentation products.

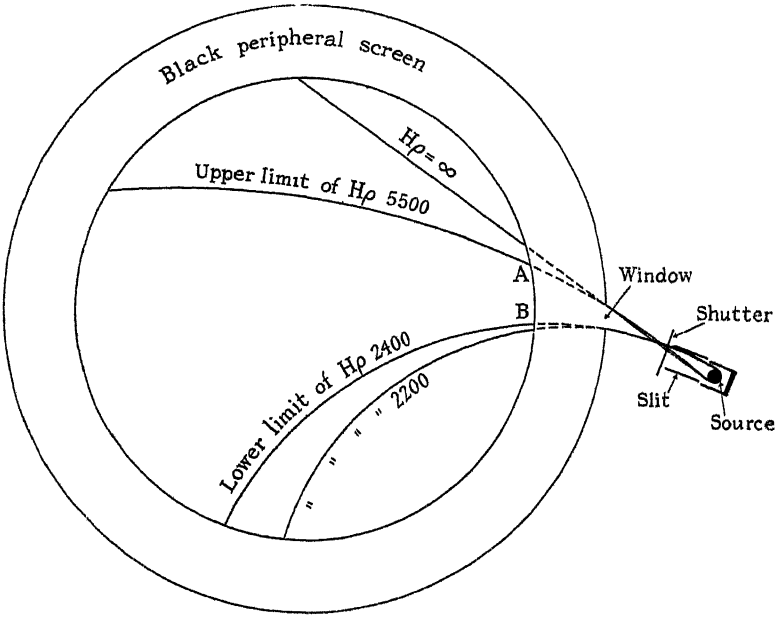

FIG. 1.

The method was tested by drawing random tracks, photographing them, computing the radius of curvature by the above method and subsequently measuring the actual curvatures. The accuracy is from 2 to 4 per cent. over the range of curvatures required in this work. It is desirable to have as little nuclear deflection of the tracks as possible, for the accuracy of the measurements will clearly depend on the length of the track which is a smooth curve. From this point of view, hydrogen would be the ideal gas to use in the chamber but the diffuseness of the tracks and the small ionisation make it very difficult to obtain good results; nitrogen was therefore used throughout.

The approximate position of the source is shown in fig. 1, which is drawn for $H = 250$ gauss. It is essential to have a rigorous criterion governing which tracks are to be counted and to abide by that criterion throughout, rejecting firmly all tracks which do not satisfy it. The initial criterion adopted was that all tracks measured must have a measurable length of undisturbed track for at least 6 cm. from the edge AB of the black screen. It is observed in the figure that all particles with $H\rho$ equal to or greater than 2200 will be fully represented under such a criterion. As a special precaution, a few photographs were taken with the magnetic field off, and the presence of a bundle of " straight" β-ray tracks in the neighbourhood of H$\rho = \infty$, showed that very fast particles would have been adequately photographed when the field was on. The fulfilment of the criterion required the rejection of about 1 in 10 tracks. The effect of this rejection on the relative numbers of particles found in different parts of the spectrum and its connection with the velocities is discussed later.

3. *Results and Discussion.*

The maximum number of particles in the spectrum is found by all experimenters to occur at about Hρ 2200. It has been shown that with the experimental disposition employed here, particles with a velocity corresponding to this value would just have been adequately represented. The lower limit of tracks investigated was therefore raised, for further safety, to Hρ 2400. One thousand tracks with Hρ greater than 2400 have been examined in detail; of these, none has been found with Hρ greater than 5500 and only five with Hρ greater than 5000. The estimated error in a single determination of Hρ in the region of the upper limit is ±5 per cent., so the results are in complete agreement with the earlier workers. The actual distribution found is shown in Table I. Each reading on the left, in the first column, gives the mean value of Hρ over a range of 400 Hρ; thus the first reading 2600 corresponds to a range 2400–2800. The second column gives, on the left, the number of tracks

Table I.

Mean Hρ.		Number of tracks.				
		Champion.		Madgwick.		Terroux.
2600		374		346		
3000		267		267		
	3200		437		451	230
3400		170		184		
3800		112		112		
	4000		165		161	161
4200		53		49		
4600		17		16·5		
	4800		24		19·5	79
5000		7		3		
5400		2		—		
	5600		2		—	33
5800 and onwards to 12,000		—		—		Total here = 106

found with velocities falling within the range indicated in the first column. The third column gives, on the left, the values estimated from Madgwick's curve, which was obtained using the ionisation method and the fourth column gives the results obtained by Terroux. For the purposes of comparison with the last-named, the intervals of 800 Hρ are used; the mean values of Hρ are represented on the right-hand side of column 1, and the corresponding numbers of tracks on the right-hand side of the other columns.

The results of Madgwick have been adjusted numerically to fit the present results at Hρ 3000; in the comparison with Terroux, the adjustment has been made to fit the present results at Hρ 4000. This value of Hρ is, for safety, much above Terroux's estimate of the value at which his particles of lower velocity are adequately represented. It is observed that the present results are in good agreement with those of Madgwick.* Madgwick's curve is reproduced in fig. 2. The present results are represented by circles and those of Terroux by crosses. This curve was obtained from ionisation measurements and somewhat uncertain data were employed in converting the ionisation readings to a representation of the number of particles with a particular value

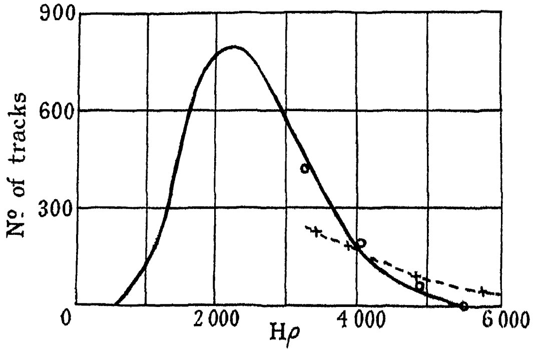

Fig. 2.

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* Let $\overline{N_r}$ be the number of particles with a given value of Hρ as given by Madgwick. Since this number is very large it may be used as a standard against which to test the statistical fluctuation of the present results. If N_r is the number of particles found at any mean value of Hρ on the present results and the whole of these results is divided into n groups, then we may apply the usual criterion that the distribution actually found is a probable one, if

$$F = (n - 1) = \frac{(N_r - \overline{N}_r)^2}{\overline{N}r} .$$

The number of groups used in this comparison is $n = 6$ over the range 2600–4600 Hρ. Hence, $F = (n - 1) = 5$ in this case. Actually, F is found to be nearly 4, so the distribution may be considered probable.

of Hρ. Further, the actual distribution in the region below Hρ 600 is very uncertain. However, using this curve for the particles of Hρ less than 3000 and fitting the present results on to the curve at that point, it is possible to form the rough estimate that less than 1 particle in 2000 is emitted with Hρ greater than 5500.

It remains to discuss the various results and to attempt some explanation of the discrepancy. First, with regard to the accuracy of the absorption experiments, Feather* has considered these in detail and concludes that certainly less than 1 per cent. of the total number of particles emitted have a value of Hρ greater than 5000. Further, in those experiments in which the existence of a band of high Hρ has been reported, it has always been considered to be of very feeble intensity. No estimate seems to have been made of its intensity relative to that of the main band and it may well be of the order indicated by the present expansion experiment. Gray and O'Leary estimate that less than 1 particle in 25,000 is emitted with Hρ greater than 8000. The only results that are in real discord with the present and previous results are therefore those of Terroux. He estimated that 4 per cent. of the total number of particles emitted had Hρ greater than 5000. Such a distribution would be in disagreement, not only with previously obtained spectral distributions but also with the experiments of Ellis and Wooster,† and Meitner and Orthmann,‡ on the mean energy of disintegration of the radium E atom as determined from the heating effect. These results give the mean energy of disintegration n good agreement with Madgwick's curve; the results of Terroux predict a mean energy definitely greater than this. Since the present method is essentially that of Terroux, a few possibilities of the causes of the discrepancy will be considered.

The adoption of a rigorous criterion for the rejection of tracks of which the curvature is doubtful, is of fundamental importance. This implies, however, a considerable amount of data, if the experimenter is to be in a position to adhere strictly to this criterion. Now, about a dozen tracks were found by the writer to have Hρ apparently greater than 5500, but on closer examination these were all found to suffer from one or more deflections due to passage near an atomic nucleus and simply to be tracks near the upper limit, which, as a result of these nuclear deflections, exhibited a spurious straightness. The total number of tracks rejected by the writer, over the whole range of spectrum, was about 100 out of a total of 1100. It is well known that, to a first approximation, the chance of a nuclear deflection for equal distances traversed by different particles is inversely proportional to the fourth power of their respective velocities. Over the range of velocities examined in these experiments, it may easily be shown that this will mean the rejection of about one and a half times as many tracks near the lower limit at Hρ 2400 as near the upper limit at Hρ 5000, if we make the criterion that only those tracks which are perfect over equal distances (say, 6 cm. from the commencement of the photograph) are to be counted.* The final correction that would have been necessary had this criterion been employed, was avoided in practice, by using the criterion that tracks near the upper limit must have the first 9 cm. of the track undisturbed and the tracks near the lower limit, the first 6 cm. This second scheme is preferable, as the use of 9 cm. of the undisturbed track, assists the accuracy of the determination of the curvatures at the higher end of the spectrum. The failure to adopt some such criterion may therefore account for part of the discrepancy. Again, the ratios of the numbers of tracks at mean Hρ 4000 and 4800 for the three experimenters, are 161 : 23·5, 161 : 21, and 161 : 79, respectively. The rapid change in gradient which Terroux observes here is taken by him to indicate a definite kink in the curve at the point Hρ 4000, but the writer suggests it may be due to incorrect fitting of the results to Madgwick's curve. If these slopes are adjusted to fit, by supposing the particles of lower velocity to be inadequately represented in Terroux's measurements, the percentage of fast tracks above 5000 Hρ falls to about one-quarter of that previously indicated. The fact that Terroux's results in these regions of lower velocities fall so much below the accepted values of other experimenters, indicates that the fit has been made too soon, even at Hρ 4000. Further, the number of tracks above these values is so small numerically that the probability fluctuations are very large and the attempt to fit them on to a smooth curve and deduce a Maxwellian tail does not seem justifiable.

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* 'Proc. Camb. Phil. Soc.,' vol. 27, p. 430 (1931).

† 'Proc. Roy. Soc.,' A, vol. 117, p. 109 (1928).

‡ 'Z. Phys.,' vol. 60, p. 143 (1930).

With regard to radioactive β-ray emitters other than radium E, it may be observed that an experiment made by Cave,† using a thin-walled radon tube at the centre of the circular pole-pieces of a large Weiss electromagnet and attempting to detect with an electroscope the fast β-particles which should

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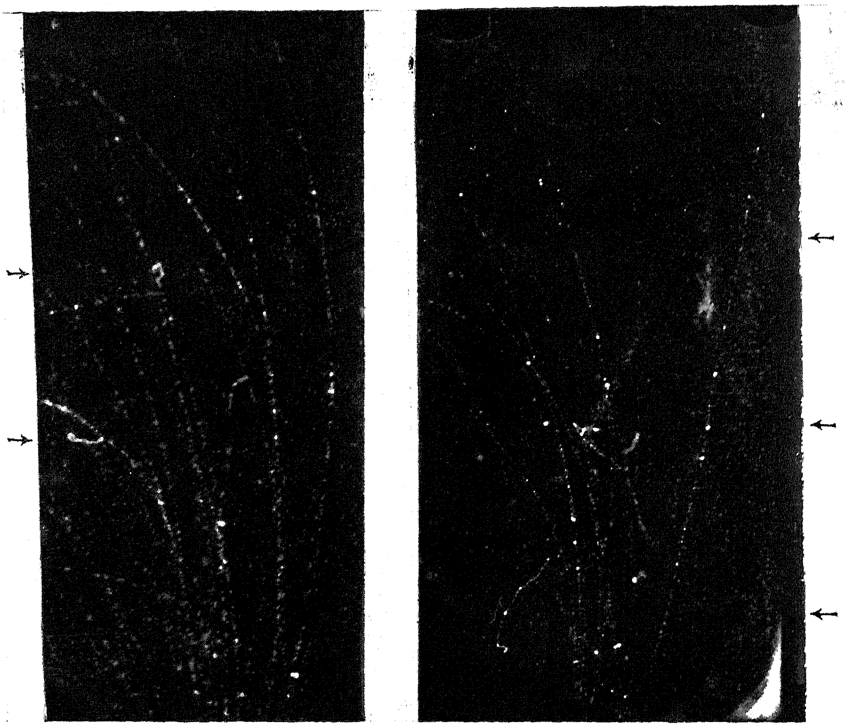
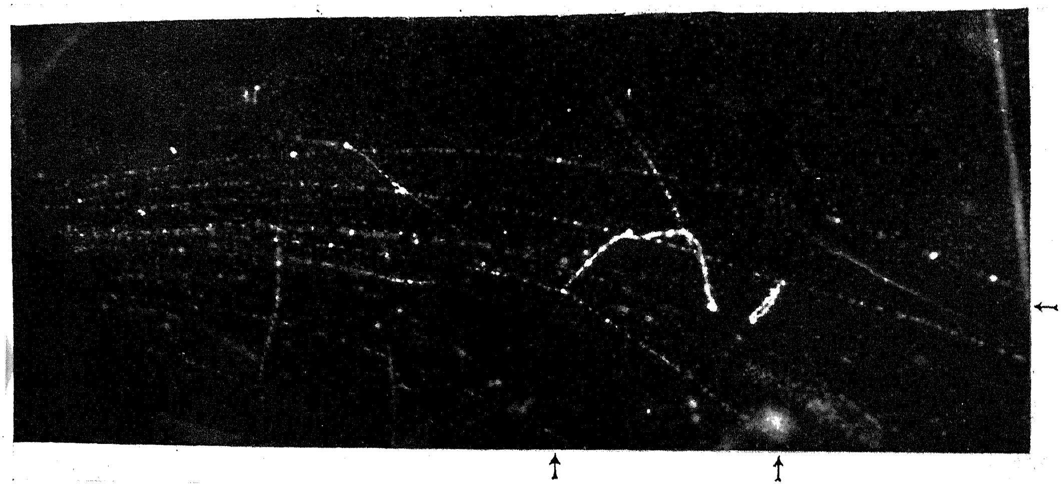
* The result of applying no correction would have been to have over-represented the fast tracks at the expense of the slower tracks and consequently the error introduced would have favoured the estimate of the number of fast tracks.

† 'Proc. Camb. Phil. Soc.,' vol. 25, p. 222 (1929).



a. *b.*

Tracks natural size at N.T.P. (*a*) This shows one of the typical β-ray "fans." There are 8 to 10 measurable tracks, which is about the maximum number which can be clearly separated. All the tracks here obey the criterion; two small collisions showing slow ejected secondary electrons are seen on the left along the lines indicated by the arrows. (*b*) This shows another typical "fan," but more particularly one of the tracks of spurious straightness in a region of the chamber corresponding to Hρ greater than 5500. The arrows indicate points at which the misleading nuclear deflections occur; the track, not obeying the criterion, was, of course, rejected.



c.

(*c*) Twice natural size at N.T.P. This shows another typical "fan" with the absence of tracks in the regions of the chamber where Hρ would be greater than 5500, that is, along the top part of the photograph. Two well-marked collisions with electrons are observed at the points indicated by the arrows; both give rise to slow secondary electrons and the difference in the ionisation along the tracks corresponding to slow and fast electrons is brought into strong contrast.

(*Facing p.* 681.)

have escaped, showed that on the average less than one of the high energy particles was emitted in every 500 disintegrations. In later experiments, Cave and Gott, using an absorption method and a radon source, estimated that the fast β-rays were less than 1 in 1000 disintegrations. Indirect evidence shows that the number of fast electrons in the radium C line Hρ 10,020 is about 20 in every 10^6 disintegrations. To return to the consideration of radium E, it is clear that expansion chamber experiments with strong sources and magnetic fields of about 1000 gauss are required to investigate the qualitative existence of any particles with Hρ greater than 5500. It is concluded at present that if they exist, the number is certainly less than 1 in 2000 of the main band.

Summary.

(1) The conditions for the production of a large number of good β-ray photographs, using an automatic expansion chamber, are discussed.

(2) The energy distribution of the β-ray spectrum of radium E is investigated from Hρ 2400 onwards, using 1000 tracks obtained with an automatic expansion chamber.

(3) The spectrum is found to end sharply at about Hρ 5500.

(4) It is estimated that less than 1 particle in 2000 is emitted with Hρ greater than this value.

(5) A review of the experimental results previously obtained with other methods is given and causes of the discrepancy previously observed by Terroux, using the expansion chamber method, are suggested.

The writer is deeply indebted to Mr. P. M. S. Blackett for continual encouragement, for invaluable advice on the experimental technique and for stimulating discussion. I wish to thank the Department of Scientific and Industrial Research for a maintenance grant which made this work possible.

Crystalline Vitamin D.

By F. A. Askew, R. B. Bourdillon, H. M. Bruce, R. K. Callow, J. St. L. Philpot, and T. A. Webster.

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(From the National Institute for Medical Research, London, N.W.3.)

Abstract.

Further purification of the antirachitic principle has been achieved by esterification of the crystalline distillation products formerly described as calciferol. The purified calciferol now obtained has an antirachitic activity twice as great as any previously recorded, and appears to be identical with the vitamin D_2 of Linsert and Windaus.

The purified product still produces toxic effects when given in excessive doses.

A simplified process is described for preparing the pure product from the irradiation products of ergosterol without distillation.

An account is given of two inactive compounds termed pyrocalciferol and sterol X.

Evidence is given of the relations between the crystalline antirachitic products hitherto described, showing that the activity of each of them is due to one common constituent. Thus the vitamin D_1 of Windaus is a compound of calciferol (= vitamin D_2) and sterol X, and the crystalline distillation products first described contained pyrocalciferol and sterol X as well as calciferol.

It is shown that the separation of a series of crystalline products, showing equal antirachitic activity, but widely different optical rotations, may be accounted for by the existence of solid solutions of the two molecular compounds, calciferol-pyrocalciferol and calciferol-sterol X. Melting-point data are given, showing that this system affords an interesting study in the application of the phase rule.

The probability is discussed that calciferol (and vitamin D_2) represent "vitamin D" in a state of approximate purity.

(*The full paper is printed in 'Proceedings,' B, vol.* 109, *pp.* 488–506.)

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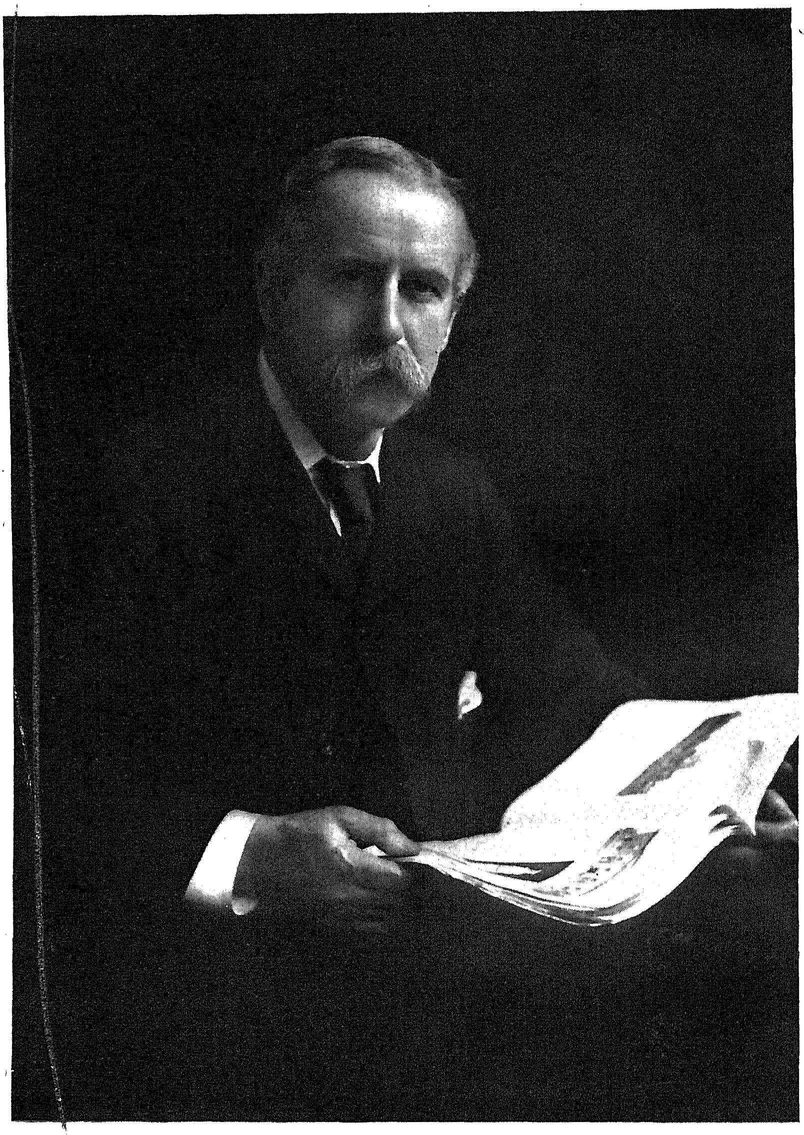

Harold B. Dixon

HAROLD BAILY DIXON—1852-1930.

Harold Baily Dixon, whose work upon gaseous explosions opened a new era in combustion research, was born in London on August 11, 1852, the second son of William Hepworth Dixon (1821–79), traveller and historical writer, who for some years was editor of the *Athenæum*. Although the family came of an old Lancashire Puritan stock, the Dixons of Heaton Royds, the grandfather of the chemist was Abner Dixon of Holmfirth and Kirkburton in the West Riding of Yorkshire, and his grandmother was Mary Cryer of those parts.

His father, William Hepworth Dixon, who was born in 1821, at Great Ancoats in Manchester, began life as a clerk in that city; but early resolving to adopt literature as a career, he became associated with a group of literary men, including Harrison Ainsworth, who were working in Manchester in early Victorian days. In 1846, at the instance of his friend Douglas Jerrold, he migrated to London; and, having early married a lively good-looking Irish girl, Marion MacMahon, they had eight children, of whom Harold Baily (second son) and Ella Hepworth (youngest daughter) achieved distinction in science and literature respectively.

William Hepworth Dixon travelled extensively and wrote many popular historical books in a lively and attractive style. His house in Regent's Park was resorted to by a brilliant group of friends, among whom were Richard Burton, Bulwer Lytton, Frederick Leighton, John E. Millais, Thomas Firth, T. H. Huxley, Henry Irving, J. L. Toole, as well as J. M. Levy, founder and editor of the *Daily Telegraph*, and a certain tall good-looking sapper called Kitchener. It has been said that, although occasionally deficient in tact, Hepworth Dixon was faultless in temper and seldom put out by any disappointment or misfortune. His sympathies were with the people, and he took a leading part in establishing the Shaftesbury Park and other centres of improved dwellings for the labouring classes. As a member of the first London School Board (1870–73) he carried a resolution, in the teeth of strong opposition, establishing physical drill in all rate-paid schools throughout the metropolis; and in 1874 he persuaded the then Prime Minister (Disraeli) to order the opening of the Tower of London to the public free of charge. Besides good looks and physical build, Harold inherited from his father the exceedingly equable temper, liberal views, and strong current of sympathy for working people and their material and intellectual welfare, which characterised his future life work at Manchester University among the men of Lancashire and Yorkshire.

His mother was a woman of innate good taste and manners, with advanced views upon the subject of women's suffrage; she went by herself to all Ibsen's plays, when they were first produced in London, and called in a lady doctor when her youngest son was born. Except, perhaps, for a certain liveliness on occasions of unusual excitement, when he would let himself go, it would be difficult to trace what influence her Irish blood may have imparted to her son Harold, who outwardly showed little sign of it, and was singularly reticent about his parents and early home-life.

In 1867 Harold was elected foundation scholar at Westminster School, from whence in 1870 he obtained a classical junior studentship at Christ Church, Oxford. As an undergraduate he was one of the most popular men of his time and threw himself into the social and athletic side of university life. He rowed in the College eight, played cricket, and obtained his blue in association football, taking part in the last game in which a University team won the English cup. He was also extremely fond of dancing. These activities so much interfered with his classical studies that he scarcely fulfilled the expectations of his tutors, and there was a danger of his University career being brought to an untimely end. Fortunately, however, in 1873, Dr. A. Vernon Harcourt induced the College authorities to transfer the young classical scholar to his care, and was thus responsible for saving for chemical science one who was destined to be numbered among its most original and lucid exponents.

Two years later Dixon graduated first-class in the Natural Science School, and was elected to a fellowship at Trinity. He then started research work with Harcourt who, some eight years previously in conjunction with Essen, had published his classical work on the rate of chemical change between solutions of hydrogen peroxide and hydriodic acid, which may be said to have founded modern chemical dynamics. Until 1879 Dixon and Harcourt worked side by side in the crypt of one of the monastic buildings on the site of which Christ Church was built. It was the room in which the first anatomical studies were carried on, chiefly upon the bodies of malefactors who had been executed within the precincts of the Castle near by. Also it was in this room that, in the 17th century, the fortunate (or unfortunate) Mary Baker was revived by the surgeons after she had been hanged for an hour. Despite such gruesome association, however, it made an admirable chemical research laboratory, being very quiet, of even temperature, and comparatively free from dust.

In 1879, Balliol and Trinity College combined in a joint scheme for the teaching of science whereby Trinity established the Millard Lectureship, to which Dixon was forthwith appointed, and Balliol provided a laboratory and lecture room. A doorway, dubbed the "scientific frontier," was opened between the two Colleges so that Trinity men might have easy access to the new rooms. Dixon then transferred his research work to a cellar in the garden quadrangle which had been used by Benjamin Brodie for his investigations upon ozone. It was damp and dark, and being devoid of any draught chamber, fumes used to rise up the staircase to the annoyance of the undergraduates having rooms above, who on one occasion were provoked to reprisals. One day, also, Dixon was so badly gassed by an accidental escape of carbonic oxide that, to the alarm of his assistant, he was in a state of complete aphasia for the next four hours. And on a third occasion, it was only his presence of mind in turning off the tap of a gasholder containing 30 cubic feet of an explosive mixture that prevented its being exploded by a flame originated by a premature spark in an apparatus which was being filled with it at the time. In 1886 he was elected to a fellowship at Balliol, and continued working there until he removed to Manchester in 1887, being assisted for some time (1883–85) by H. B. Baker.

It was at the instigation of Vernon Harcourt that Dixon commenced studying gaseous explosions in 1876; although, curiously enough, two years previously (October 2, 1874) his father's house in Regent's Park, London, had been completely wrecked by concussion waves from an explosion of gunpowder on the Regent's Canal near by.

During the sixty years which had elapsed since Humphry Davy's pioneering work on the subject, only R. W. Bunsen amongst chemists had much explored it, and for twenty years his results had been accepted without question as authoritative. More particularly the results of Bunsen's experiments (1853) on the explosion of mixtures of electrolytic gas with increasing amounts of carbonic oxide were held to be inconsistent with the principle of "mass action" enunciated by Berthollet in 1805, and led to the erroneous view that a continuous alteration in the composition of such a gaseous medium produces a discontinuous ("*per saltum*") alteration in the course and products of its explosion.

In the year 1877, during the course of a research primarily undertaken to test Bunsen's conclusion, Dixon made his epoch-making discovery that the prolonged drying over phosphoric anhydride of a mixture of carbonic oxide and oxygen in combining proportions renders it non-explosive when subjected to electric sparks of an intensity sufficient to ignite readily an undried medium. He first announced it in a paper to Section B of the British Association at Swansea on August 28, 1880 ('B.A. Reports,' 1880, p. 503) on which occasion he demonstrated it experimentally, adding that although the smallest addition of steam, hydrogen or ether vapour to the phosphoric anhydride-dried $2CO + O_2$ medium rendered it explosive, neither dry nitrogen nor dry carbonic acid nor dry cyanogen had any effect, from which (as he said) "it appears probable that the oxidation of carbonic oxide is really caused by the alternate reduction and oxidation of water molecules, according to the equations :—

(i) $CO + H_2O = CO_2 + H_2$

(ii) $2H_2 + O_2 = 2H_2O$."

Subsequently Dixon proved that the speed of flame in a $2CO + O_2$ explosion, whether during the initial phase of uniform slow movement or even after "detonation" had been set up, increases with the moisture content of the medium, up to "saturation" at about 35° C. when about 5·6 per cent. of it is present, a result which has since been confirmed by other investigators.

This discovery aroused world-wide interest and opened up a new field of chemical investigation which ever since has continued to attract workers from all quarters, and still yields abundant fruits. For, as Dixon was wont to say, "it loosed a hare which, though since pursued by the hounds in full cry, is still uncaptured."

For many years much controversy raged round various chemical theories, including the one originally favoured by Dixon, which from time to time were put forward to explain the comparative inertness of dry carbonic oxide oxygen media, and many important experiments were made in attempts to discriminate between them. M. Traube and Lothar Meyer in Germany, Beketoff and Mendeleeff in Russia, H. E. Armstrong as well as Dixon and his pupils in this country, figured prominently in the discussions. Nowadays, while not rejecting the well-known chemical interactions both of steam and hydrogen peroxide with carbonic oxide as partial explanations (especially when massive proportions of such "promoters" are present), there is a growing consensus of opinion favouring a physical explanation of the phenomenon, which latterly Dixon himself more and more inclined to. Indeed, his last published words upon the subject (in reviewing some experiments upon the influence of a strong electric field upon the combustion of a rigidly dried $2CO + O_2$ medium) were that "it was evident that the resistance to combination offered by the dryness of the gases could be overcome by the electrostatic field . . . (so) that the problem presented by the burning of this gas has become one of the most interesting in physical chemistry."*

Dixon's early Oxford researches (1876–81) besides proving, *contra* Bunsen, the validity of Berthelot's "law of mass action"—a conclusion which was simultaneously established by the independent work of Horstman in Heidelberg—laid a firm and lasting foundation upon which much later work on equilibria in reversible gaseous interactions has been built.

Until the year 1880, on the strength of some measurements made by R. W. Bunsen in 1857, it was generally believed that gaseous explosions travel at rates not exceeding a few metres per second only; but on July 5 of that year a disastrous explosion in a 36-inch gas main in Percy and Charlotte Streets and Fitzroy Square near Tottenham Court Road, London, involving the loss of two lives and much damage to property in the neighbourhood, afforded conclusive evidence of much higher speeds. Vernon Harcourt, who had been called in to investigate the matter, suggested to Dixon the desirability of his undertaking a systematic investigation of the rates of propagation of flames in gaseous explosions generally, which he forthwith began. He had not got far with it, however, before Berthelot and Vieille announced (1880) their discovery of the high constant flame speeds finally attained on the development of " l'onde explosive " (" detonation ") in gaseous explosions. This revelation, together with the appearance of Mallard and Le Chatelier's classical "*Recherches sur la combustion des mélanges gaseux explosifs*" in 1883, showed that the comparatively slow flame speeds observed and measured by Bunsen apply only to the mild and usually short initial phase of such explosions.

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* 'Nature,' vol. 129, p. 582 (1929). Also a complete review of 50 years' work (1880–1930) on the subject is given in the Third Liversidge Lecture before the Chemical Society, by one of us (W. A. B.)

Working on parallel lines with these French savants during the next twenty years, Dixon so successfully developed the methods initiated by them that he soon became a leading authority upon the subject. In 1893 he gave the Bakerian Lecture on " The Rates of Explosion in Gases," and nine years later published in the 'Philosophical Transactions' of the Society a brilliant memoir embodying his photographic researches on " The Movements of Flame in the Explosion of Gases."

The method adopted by Dixon for measuring " rates of explosion " (" detonation ") in gaseous explosions followed closely in principle that originated by Berthelot and Vieille; but his determinations were more systematic, and in some cases more accurate, than theirs. They concluded that the velocity of the " explosion wave " is quite independent of the material and diameter of the tube employed, provided that a certain small limiting diameter is exceeded, and independent of the pressure; the last-named conclusion, however, Dixon subsequently found erroneous by showing the rate increasing slightly with pressure, at least up to two atmospheres. They termed it, for a given explosive mixture "*une propriété fondamentale ; car elle établit que la vitesse de propagation de l'onde explosive est régie par les mêmes lois générales que la vitesse du son.*" And, assuming that it equals, or approximates closely to, the mean velocity of translation of the molecules at the moment of combination, supposing them to retain all the heat developed in the reaction, they proposed the formula

$$v = 29{\cdot}354 \sqrt{T/d},$$

where T = the maximum temperature (abs.) reached in the explosion, and d = density of the products of combustion referred to air.

They further assumed (i) $T = Q/6{\cdot}8n$, where Q = the heat liberated by the chemical change involved in the propagation of the wave, and n = the number of " molecular volumes " taking part therein; also that (ii) the gases are heated at *constant pressure*, (iii) the specific heat of a component is the sum of the specific heats of its constituents, and (iv) " dissociation " hardly affects the propagation of the wave, because of its extremely short duration and the high pressures developed therein. Although it so happened that the velocity (2810 metres per second) which they actually found for electrolytic gas ($2H_2 + O_2$) came very near the 2831 metres per second calculated on the foregoing assumptions, most of their other observed experimental values fell short of the so-calculated values, and notably the observed 1089 as compared with the calculated 1941 metres per second in the case of a $2CO + O_2$ medium. This led them to regard their formula as "provisional" only, in the same sense that it gave a *limit* representing the *maximum* possible rate of propagation and subject to diminution in various ways, so that in many cases (as they said) "*la combustion se propageant alors de proche en proche suivant une loie beaucoup plus lente.*"

While adopting the "sound wave" theory of Berthelot and Vieille in principle, Dixon subjected it in his Bakerian Lecture to a searching criticism in detail, more particularly in regard to certain of their assumptions, with which he disagreed. He sought to modify it so as to make it better fit the facts by supposing that (i) the explosion wave is carried forward by movements of molecules of density intermediate between that of the products of combustion and that of the unburnt gases, (ii) the gases are heated at constant volume (not constant pressure), (iii) the temperature of the gas propagating the wave is double that due to the chemical reaction alone, and (iv) that the velocity of a sound wave is only 0·7 of the mean velocity of the molecules in the medium through which it is passing.

Even when so modified, however, the "sound wave" theory predicted in a number of cases (*e.g.*, most undiluted detonating mixtures) rates of explosion so much higher than those actually observed—*e.g.*, for undiluted electrolytic gas the "calculated" rate was 3416 as compared with the found value of 2830 metres per second—that eventually it had to be abandoned. Indeed, both its French authors and Dixon had quite erroneously assumed that the heat capacities of gases to be independent of temperature, while Dixon overestimated what he thought to be the limiting influence of "dissociation" in the wave. For, in 1910, he confessed quite frankly "I do not believe to-day in the truth of my working hypothesis of the explosion wave. It embodied a number of assumptions, some of which I have myself shown to be erroneous. The theory of the explosion wave is not to-day dependent on the hypothesis of Berthelot and myself." And at the same time he expressed his conversion to the newer views advanced independently by Hugoniot (1887–88), D. L. Chapman (1899), Vieille (1899–1900), and E. Jouguet (1906), according to which "detonation" is essentially a "shock wave" propagated through a medium which is discontinuous in the vicinity of the wave front, in the sense that an abrupt change in pressure and density in the vicinity of the wave front is propagated and maintained from layer to layer by the adiabatic ignition of the explosive medium, a conception which has now superseded the former " sound wave " theory.

The great and permanent value of Dixon's work in this connection really lay both in his accurate and systematic measurements of " rates of explosion " (" detonation "), most of which were set forth in his Bakerian Lecture (*q.v.*), and in certain important conclusions which he deduced therefrom regarding the chemical reactions actually concerned in the propagation of the wave. Thus, for example :—

(i) His observed rates for the following cyanogen mixtures :—

$$\frac{C_2N_2 + O_2}{2728} \left\{ \begin{array}{cc} \dfrac{C_2N_2 + 2O_2}{2321} & \dfrac{C_2N_2 + 3O_2}{2110} \\ \dfrac{C_2N_2 + O_2 + N_2}{2398} & \dfrac{C_2N_2 + O_2 + 2N_2}{2166} \end{array} \right\} \text{metres per second}$$

showed that the gas burns in two well-defined stages, namely (*a*) primarily to carbonic oxide in the wave itself, and (*b*) afterwards to carbon dioxide behind it.

(ii) His observed rates (at 10° and 760 mm.) for the following hydrocarbons with varying proportions of oxygen showed that (*a*) there are distinct stages in the explosive combustion of a hydrocarbon, and (*b*) *in the wave itself*, the carbon burns primarily to carbonic oxide, which afterwards burns to carbonic anhydride in the rear of the wave, the rate of explosion for a mixture containing sufficient oxygen for *complete* combustion being always much less than that for one containing only sufficient oxygen to burn the carbon to carbonic oxide ; thus he found :—

Methane-Oxygen Mixtures.

$CH_4 + O_2$	$CH_4 + 1\frac{1}{2}O_2$	$CH_4 + 2O_2$	
2528	2470	2322	metres per second.

Ethylene-Oxygen Mixtures.

$C_2H_4 + O_2$	$C_2H_4 + 2O_2$	$C_2H_4 + 3O_2$	
2507	2851	2368	metres per second.

Acetylene-Oxygen Mixtures.

$C_2H_2 + O_2$	$C_2H_2 + 1\frac{1}{2}O_2$	$C_2H_2 + 2\frac{1}{2}O_2$	
2961	2716	2391	metres per second.

It was in connection with his foregoing determinations of the rates of explosion of hydrocarbons, which were mostly made in Manchester during

1891–92, that Dixon and his collaborators rediscovered the extremely important fact, first observed by Dalton in 1803–04 but afterwards long forgotten, that on explosion an equimolecular mixture of ethylene and oxygen yields about twice its own volume of carbon monoxide and hydrogen, in accordance with the equation

$$C_2H_4 + O_2 = 2CO + 2H_2.$$

This rediscovery, reinforced by similar observations by Smithells and Ingle (1892) upon the interconal gases of aerated hydrocarbon flames, and by the experiments of W. A. Bone in conjunction with B. Lean and J. C. Cain on explosions of ethylene or acetylene with less than their own volumes of oxygen, finally laid the dogma of the preferential burning of hydrogen in hydrocarbon flames, which had been unquestionably accepted among chemists as an article of faith for sixty years previously, thus clearing the ground for modern views of the mechanism of hydrocarbon combustion.

In 1886, while in the middle of his work upon "rates of explosion," Dixon was appointed to succeed Sir Henry Roscoe in the Chair of Chemistry at Owens College, Manchester; and this he occupied until his retirement in 1922, when he became honorary professor at the University, while continuing his researches right up to the day of his death. And it was in Manchester that his powers and life work came to fullest fruition and that his greatest influence was exerted.

Under Roscoe and Schorlemmer the Manchester School of Chemistry had become so famous and dominant in the country that many predicted its reputation would inevitably suffer by the former's supersession by a comparatively young and untried Oxford don. But Dixon's outstanding administrative gifts, his devotion to experimental research, his brilliance as a lecturer, his power of arousing in his students the true spirit of enquiry, and the way in which he always identified himself with the social and athletic sides of the College and University, proved more than equal to the task, so that the reputation of the School continually increased under his leadership. He was indeed the *beau ideal* of a university professor.

When Dixon went to Owens College in 1887, its professoriat included Horace Lamb (Mathematics), Balfour Stewart and A. Schuster (Physics), Osborne Reynolds (Engineering), Carl Schorlemmer (Organic Chemistry), W. C. Williamson (Botany), A. Milnes Marshall (Zoology), Boyd Dawkins (Geology), Robert Adamson (Philosophy), A. W. Ward (History), A. W. Wilkins (Latin), and Alfred Hopkinson (Law). His own chemical staff comprised Carl Schorlemmer, G. H. Bailey, Harry Baker, J. B. Cohen and Watson Smith; and a year later G. J. Fowler and A. Harden joined it. It was probably at the time the strongest chemical teaching staff in the country, and the splendid lecture theatre and laboratories which had been built fifteen years previously under Roscoe's supervision were then unsurpassed.

It did not take Dixon long to settle down and get to work in such a congenial environment, which powerfully stimulated and developed his scientific and administrative powers. And he soon attracted round him a band of enthusiastic students and workers, with whose co-operation he founded his Manchester School of Combustion Research. His first research assistants were H. W. Smith and G. H. Turpin (1888), followed by W. A. Bone and B. Lean (1891), E. H. Strange and E. Graham (1894), and E. J. Russell (1896), and later by R. H. Jones and L. Bower, all of whom collaborated with him in the experimental work on gaseous explosions during the period 1888–1903, the results of which were ultimately embodied in two *magna opera* in the Philosophical Transactions of the Society in 1892 and 1903, as well as in other papers published in the Journal of the Chemical Society between those years.

Before dealing with his Manchester researches, something should be said about his direction and development of its great chemical school. In some respects his start off was not altogether auspicious. For under his predecessor, Roscoe, who for some years (1852–56) before his appointment to Manchester in 1857 had been closely associated in research with Bunsen in Heidelberg, the school had been steeped in Bunsen traditions, and naturally enough at first some of the old hands did not take very kindly to the succession of an Oxford don who not only plumed himself on having upset Bunsen's conclusions about gaseous explosions, but also had quite other ideas about teaching, and left the supervision of routine laboratory work mainly to his subordinates. This feeling, however, soon died down when they discovered how keen Dixon was upon giving everyone ample opportunities for research, and how great were his gifts as a leader and administrator. And henceforth he was strongly supported by all concerned, and success was both great and unbroken.

In 1892 his colleague Schorlemmer died and was succeeded by the late William H. Perkin, jun., whose dynamic personality and unrivalled technique infused such new vigour into the organic side of the school that soon its laboratories so overflowed with students and researchers that extension of its buildings and equipment became necessary. The successive additions of the "Schorlemmer," "Schunck," and "Morley" laboratories barely sufficed to accommodate the ever-increasing crowd of workers. Work went on busily day and night during term-time and vacation, throughout the whole year, in never-ceasing activity. The fame of it spread into many lands and "fired the heather" throughout the North. The youth of Lancashire and Yorkshire "caught on" and joined up in their scores. There is a spirit in the bleak Northern moorlands—

"*where th' east wind blows snell an' keen*"

—that knows great leadership and "scents battle from afar," and in the nineties Dixon and Perkin captured it for chemical science. Although differing widely in temperament, up-bringing and outlook, they shared a common enthusiasm for experimental research, gave each other constant and ungrudging mutual support, and proved an ideal combination for the development of a great chemical school. In 1913 they were joined in its professoriat by A. Lapworth, who eventually succeeded Dixon on his retirement in 1922. Of their lieutenants and pupils, W. A. Bone, H. C. H. Carpenter, D. L. Chapman, J. B. Cohen, A. W. Crossley, A. Harden, N. Haworth, J. W. Mellor, F. L. Pyman, Robert Robinson, E. J. Russell and J. F. Thorpe subsequently became Fellows of the Society; P. J. Hartog, B. Lean, Norman Smith and G. S. Turpin achieved distinction in educational affairs; while G. W. Andrew, G. H. Bailey, E. Bury, H. G. Colman, T. Ewen, G. F. Fowler, H. Hartley, D. S. Jerdan, H. Levinstein, R. Lessing, G. P. Pollitt, R. S. Slade and R. V. Wheeler, to mention a few only out of many, subsequently made their mark in industry and technology.

After completing his work on rates of explosion in the early nineties, Dixon's researches (though comprising also the combustion of both carbon and carbon disulphide, as well as further experiments upon the influence of moisture in the combustion of carbonic oxide) were chiefly photographic studies of flame movements in explosions, in which work he had the collaboration of first of all E. H. Strange and E. Graham, and afterwards R. H. Jones and L. Bower. Although the method adopted, namely, that of photographing a horizontally moving flame upon a film moving vertically with known velocity—was in principle the same as had been originated by Mallard and Le Chatelier in 1880–83, it was so vastly improved and developed in detail as to become a very refined and accurate method of flame analysis. It was first described in a paper "On the Explosion of Cyanogen" communicated to the Chemical Society in 1903; but the memoir embodying the full results thereof appeared in 'Philosophical Transactions' for 1903. Meanwhile both Berthelot and Le Chatelier, who had been working on similar lines in France, published papers on the subject in 1899 and 1900.

It is impossible in the short space at our disposal to give any adequate idea of the wealth of information contained in the seventy or more photographs of explosion flames included in Dixon's 1903 memoir; indeed, the only way for anyone to understand their value is to study them closely in detail. Suffice it to say that the whole course of a gaseous explosion, from its initial phase of slow uniform flame movement up to its culmination in detonation was photographically analysed with great precision. Not only were the influences of compression waves and the collision of detonation waves illustrated, but discoveries were made of (i) the backward "retonation wave" which is always set up when detonation is determined in a gaseous explosive medium, and (ii) the "reflexion waves" which arise when a detonation wave is either arrested by the closed end of a tube or momentarily retarded on passing a constriction in it. Similar discoveries were simultaneously made independently by Le Chatelier in France, so that the years 1900–03 saw a remarkable resuscitation of the interest aroused twenty years previously by the kindred researches of the same masters.

Dixon's third principal line of research, which chiefly occupied him after 1903, and in which he was assisted by H. F. Coward, J. M. Crofts, L. Bradshaw, C. Campbell and others, was concerned with the " ignition temperatures " of explosive gaseous media, which he was the first to determine with any real degree of accuracy. Previous attempts, notably by V. Meyer and pupils in Germany, and Emich in Austria, had been frustrated by the considerable amount of pre-flame surface-combustion which always had occurred in their experiments before the explosive medium as a whole had been raised to the true ignition point. To obviate this source of error, Dixon and Coward devised their well-known " concentric tube " method in which streams of combustible gas and air (or oxygen) were separately heated to the temperature of the medium before being allowed to mix. In this way, the "ignition range" at atmospheric pressure of hydrogen was found to be 580°–590° in both air and oxygen, of moist carbonic oxide 644°–658° in air and 637°–658° in oxygen, of acetylene 406°–440° in air and 416°–444° in oxygen, and so on. Paraffin hydrocarbons, such as methane and ethane, were similarly found to have much wider " ignition ranges," *e.g.*, that of methane was 650°–750° in air and 556°–700° in oxygen. Later on, after it was discovered that the earlier results had been affected by the fact that when an explosive mixture is rapidly heated even to its " ignition point " an appreciable " lag " may occur in the actual appearance of flame, the concentric-tube apparatus and procedure were modified so as to control and determine such " lag." In this way it was found that the longer the " lag " allowed, the lower the resulting ignition temperature. Thus, for example in the case of hydrogen at atmospheric pressure for a " lag " of 0·5 second only the " ignition temperature " was 631° in air and 625° in oxygen, respectively, but on allowing a " lag " of 10 second temperatures of 588° and 582° only were required.

In 1906–07 H. G. Falk, acting on a suggestion by W. Nernst, had endeavoured to determine the ignition temperatures of various gaseous explosive mixtures under adiabatic compression, by compressing them in a steel cylinder the piston of which was suddenly driven in by means of a falling weight. And, finding that with hydrogen-oxygen mixtures the equimolecular required the least degree of compression (corresponding with a temperature of 518°) for its ignition, he concluded that hydrogen peroxide, and not steam, is the first product of the reaction.

Dixon, who never believed in any " peroxide " theory of combustion, at once took up the matter in conjunction with J. M. Crofts, and had no difficulty in proving, not only that Falk's experimental method had been faulty in that the piston had not been stopped at the beginning of the pre-flame period, but also that two of his assumptions were generally invalid. And on publishing their own experiments in 1914, they had no difficulty in showing that his conclusion regarding the ignition of hydrogen-oxygen mixtures was entirely wrong. They showed that (i) the true ignition temperature of electrolytic gas under adiabatic compression is 526°, and (ii) whereas successive dilutions of it with either hydrogen or nitrogen continually raise, dilutions with oxygen continually depress, the ignition temperature, such depressions continuing long after the $H_2 + O_2$ ratio has been passed. At the time, this unexpected result suggested to them the formation of some active "polymeride" of oxygen under the experimental conditions; but nowadays it would not be regarded as indicating more than some prior "activation" of oxygen as a prior condition of the combustion.

Dixon continued his work on ignition phenomena right up to the end and further discovered (*inter alia*) that "ignition temperatures" of gaseous media are, or may be, profoundly affected by the presence of small amounts of impurities therein. Thus he found, for example, that whereas the presence of small quantities of oxides of nitrogen lowers, that of iodine vapour materially raises, the ignition temperature. And it was upon experiments arising out of the action of iodine, which has important bearings upon the prevention of explosions in coal mines, that Dixon was engaged in his laboratory a few hours only before his sudden death at Lytham in the afternoon of September 18, 1930, thus leaving an "unfinished symphony" for his pupils to complete.

Although Dixon devoted his scientific life to the study of combustion, other problems in inorganic chemistry sometimes occupied his attention. Among them the one which showed a notable advance on any preceding work on the subject was his determination with E. C. Edgar, of the atomic weight of chlorine ('Phil. Trans.,' p. 169 (1905)). A few years before, Edward Morley had determined, with an accuracy never before approached, the direct ratio of the combination of hydrogen with oxygen. Since very many atomic weights depend on the synthesis or analysis of oxides, Morley's result led to the correction of a large number of these constants. But, in 1905, the atomic weights which depended on the analysis of their chlorides were also numerous and the determination of the ratio of hydrogen to chlorine was therefore important. The weighing of chlorine was the great difficulty. It was solved by liquefying the gas in a weighed bulb and weighing it at the ordinary temperature. Since no ordinary glass tap would stand the pressure, the plug always blowing out, Dixon had taps made in which the slope of the plug was reversed, so that the greater the pressure, the tighter was the tap. This ingenious modification enabled a most concordant series of values to be obtained, and it is interesting to note that, after 26 years, Dixon and Edgar's number for the atomic weight of chlorine still stands.

Besides being both a great exponent of the experimental method in science and an able administrator, Dixon shone brilliantly as a lecturer, teacher and master trainer of those who were privileged to be his pupils in research; and it was as such that the influence of his personality was most markedly felt. For he prided himself most on having founded an English School of Combustion Research embodying the traditions of Robert Boyle and Humphry Davy with whom he ranks in apostolic succession. In writing to one of us on August 26, 1927, about the publication of "Flame and Combustion in Gases," which had been dedicated to him, he said "I think you know that I regard the chief reward of my work to lie in the fact that when I started fifty years ago to repeat Bunsen's experiments, no one in England seemed to care about the burning of gases, and now there is an active English School largely made up of old students . . . really keen on the fundamental study of gas reactions." And it is worth while considering how this resulted from his work and influence.

First of all, his lectures, distinguished as they always were by great clearness, logical presentment and wealth of experimental illustration, aimed chiefly at expounding principles, as exemplified by the researches of great masters, and at arousing in his students the true scientific spirit of enquiry. One of his most distinguished pupils has recently testified to us that "his account of the classical investigations showed how discoveries were made, the ideas at the back of the minds of the investigators, and the methods whereby they overcame difficulties. Personally, I found this method most inspiring, and far better than any exposition of the results. As he used it, the historic method was a splendid instrument for training research pupils, and it undoubtedly helped all his students." Indeed, no one privileged to hear his lectures could fail to be impressed by the acumen and power of a great teacher.

Next, he had an unusually sound critical faculty and complete mastery of clear exposition in the best and most concise of English. In his earlier days in Manchester, while yet his school was of such dimensions as allowed it, he would get his "first-year honours" pupils to write him weekly essays on some subject arising out of his lectures, and in a special weekly tutorial he dealt with their efforts, reading out and criticising passages from them. Each of his "third year" students was required, about twice each term, to write an exhaustive essay upon some subject of the day, after reading and abstracting all the principal researches upon it; and it was Dixon's invariable custom privately to go through each composition with its author, sometimes even spending hours in criticising and discussing it. He never let any weakness in argument, inconsistency in statement, or loose expression go by uncorrected, and was untiring in his efforts to evoke good literary style and habits. Not only so, but on occasion he would ask a senior research assistant to lecture to him on the subject of an essay, in order to train him in its verbal exposition. Many of his pupils owed a great deal to him in these respects.

Lastly, his singularly clear and penetrative mind referred everything to the final test of a well-ordered experiment, critically carried out without hurry or bias, and with the results checked at every conceivable point. He insisted upon everything being done with the greatest care and circumspection and afterwards subjected to the most vigorous examination. At all times he was unsparing in the guidance of his experience and unrelaxing in impressing on all concerned the paramount importance of accuracy and truth, together with the highest standard of experimental work. He always held that what apparently are the simplest cases of chemical change are fundamentally the most obscure and worth while investigating. His method was first of all to get at the facts, with all due precautions against possible errors, then to consider critically their bearing on the matter involved, and to advance the experimental proof step by step, by a process of exclusion, until it had been narrowed down to a single issue which finally had to be tested in every possible way. And, at the end of it all, he would often constitute himself the *advocatus diaboli*, trying his hardest to upset the verdict. Not long ago he remarked to one of us that he had never seen any law or theory relating to flame and combustion which could not either be disproved or shown inadequate, so varied and complex are the possibilities, adding "I know no law of flame, nor want to." For, eschewing all rash speculation, and attaching little importance to theories save as working hypotheses, the dry light of science shone throughout all his work, and he had a singular felicity in choosing just the right words in expounding it. Being associated with him in research meant, not only having to excel as a craftsman, but undergoing an exacting mental discipline such as only strong minds could stand; but to them it became the way of understanding.

He always endeavoured to transfer to his teaching staff those of his research pupils and assistants whom he thought most highly of, and to retain them there for some years. Their pay was wretchedly poor, and he did nothing to improve it, regarding it as part of a salutary discipline; but in compensation he arranged the duties so that each one had half his time for research, and was given all possible facilities for pursuing it independently. And he was against anyone accepting a better post outside until research had become his ingrained habit and he had established some reputation as an independent worker. Hard and long as was the discipline, everyone who underwent it was conscious of being handled with real appreciation and understanding, however austerely, and ever afterwards was thankful for it.

From Manchester many of his pupils went forth to plant research colonies in other centres, and in later years he took great delight in visiting them. So keen was his interest, that he would journey any distance to see a new experiment, or correspond at any length about it. In visiting his pupils' laboratories, he would watch everything with a most critical eye, quick to take in every point of an experiment, and to detect the slightest flicker of a flame; but when he had convinced himself of the genuineness of a new result, his appreciation of it was both deep and sincere. At times, on such occasions, he would sit up to well-nigh daybreak discussing the results, and comparing them with his own; and always he gave generously of his experience, whether personally or by letter.

Although Dixon always took an active share (as member of its Court and Council) in Manchester University affairs, and managed his own Department of it supremely well, it would not be easy to point to anything which he specifically influenced except the social and athletic sides of student life, in which he always took the greatest interest, and the work of the Joint Matriculation Board of the Northern Universities, of which he was Treasurer for fifteen years. He was prominent among those who organised the Faculty of Science in the newly constituted University in 1903, after the break up of the old federal Victoria University and the granting of separate charters to Manchester, Liverpool and Leeds. It was mainly through his energy that the present splendid University athletic ground and pavilion at Fallowfield were secured.

Outside the University, Dixon played a notable part in the educational affairs of Manchester and Salford. He took a great interest in the Manchester High School for Girls, and in its appendage the Pendleton High School, both of which owe a tremendous debt to him. Also, for many years he was co-opted member of the Salford Education Committee, Chairman of its Higher Education Committee, as well as of its Royal Technical College and some of its secondary schools; all these positions he continued to fill until the end with conspicuous success and great advantage to the public. Latterly he devoted much time to the establishment of the new Queen Mary's Secondary School for girls at Lytham, and was returning from a meeting in this connection at Lytham when he was suddenly taken ill and died.

Dixon was elected Fellow of the Royal Society in 1886, was the Bakerian Lecturer in 1893, served on its Council 1902–04 and was awarded one of its Royal Medals in 1913. In 1922 the University of Manchester conferred upon him its D.Sc. *honoris causa*, the University of Prague having similarly conferred its Ph.D. some years previously. In view of the outstanding importance of his scientific work it may seem strange that these were the only honorary academic distinctions conferred upon him; but Dixon was markedly indifferent about such honours, and never sought after them.

He presided over the Chemical Section of the British Association at its Oxford Meeting in 1894, when he delivered a memorable address entitled "An Oxford School of Chemists," in which he charmingly reviewed the work of Robert Boyle and his pupils, Robert Hooke and John Mayow. He was President of the Manchester Literary and Philosophical Society during 1907–09, and of the Chemical Society during 1909–11. He was always ready to serve the public interest. In 1881 he made experiments for the Board of Trade on standards of light to be used in photometry, and three years later he made photometric measurements upon various illuminants at the experimental lighthouses erected by Trinity House on the South Foreland. He served on the Royal Commission on Explosions of Coal-dust in Mines (1891–94) and on Coal Supplies (1902–05); also he was a member of the Home Office Executive on Explosions in Mines (1911–14), and since 1927 acted as Supervisor of Researches on the Ignition of Gases under the Safety of Mines Research Board. During the War he was Deputy Inspector of High Explosives for the Manchester area and Chairman of the Ministry of Labour Selective Committee for the North-Western District, for which services he was appointed C.B.E. in 1918.

Amid his manifold other interests, Dixon never lost his early love of the classics, and while voyaging to South Africa with the British Association in 1906 he produced for private circulation a verse translation of the Odes of Horace, which for scholarly treatment and real feeling could scarcely be surpassed. Indeed, Horace and Omar Khayyâm were his favourite authors, and he was filled with the spirit of the "Novum Organon," of which his scientific work was the fruit.

As a boy, Harold Dixon was very handsome, his portrait being painted by Thomas Firth, R.A., and his head modelled by Bailey the sculptor, in both cases at the artists' request. Of medium height, with well-knit frame, throughout his life his was an arresting face and bearing in any social assembly. In outward features he bore a strikingly close resemblance to his great contemporary Berthelot, than whom he was 25 years younger. Indeed, at one time it was difficult to distinguish the two when they were together.

He was brilliant in conversation, and as an after-dinner speaker; a man of the world, he had much sympathy with the weakness of human nature, but was intolerant of all shams and bores. He had a remarkably equable temperament and *sang froid,* always showing great coolness and presence of mind in time of danger. A story is told how once during 1889 in Manchester, when he and his assistant had miraculously escaped injury from the accidental explosion late one afternoon of the contents of a 10 cubic foot holder full of electrolytic gas which wrecked the room in which they were working, Dixon went out to a dinner party some three hours afterwards, and on being asked by a lady whether he had heard of "that dreadful accident to a poor professor at Owens College," replied "Yes, I did hear a report!"

Although Dixon continued to play both cricket and tennis well into middle life, his chief physical recreation was mountaineering in which he excelled. He climbed much with J. N. Collie and Milnes Marshall, being one of the party when the last-named lost his life on Scawfell on December 31, 1893. During 1890–93 he accomplished more than twenty first-class climbs in the

Alps, and was elected to the Alpine Club in 1894. Afterwards, in 1897, he climbed in the Selkirks, Canada, making first ascent of both Pollux and the Dome, and the second ascent of Castor, with C. E. Fay and others. Also, in the Canadian Rockies, he made the first ascents of Mounts Lefroy and Gordon with C. E. Fay, Norman Collie and C. S. Thompson.

Although of a kindly disposition, and always most friendly towards his colleagues and assistants, being ever ready with practical sympathy and help in times of need and trouble (as many have testified), he was singularly reticent about himself and masked his real feelings. It was easy for a colleague or assistant to establish and continue friendly relations with him, but difficult to penetrate within his outer ring of electrons. The experience of one of his Manchester staff who said " I didn't feel after thirteen years acquaintance that I knew him any better than after three months," would (we think) be shared by many others. Even to those of us who knew him longest and best, it was rarely (if ever) that he revealed anything of his more intimate self. And while hosts of his old pupils will ever remember him with deep affection and gratitude, most of them will still wonder whether they ever really knew him at all.

He was twice married, first in 1885 to Olive Beechey Hopkins of Montreal, who died in 1917, and by whom he had a son and a daughter; and then in 1918 to Muriel Kinch of Yelverton (South Devon) who survives him, and by whom he had a daughter. All three children also survive him.

His mental powers were maintained quite unimpaired right up to the end which came suddenly at Lytham on September 18, 1930. Only a few weeks before, when paying what proved to be his last visit to the laboratories of one of us (W. A. B.) at the Imperial College, London, he spent most of the day seeing and discussing some new photographic experiments on the development of " detonation " in gaseous explosions. He examined the resulting flame photographs intently with all the old critical keenness of his practised eye. The hours sped by almost unnoticed; at last, suddenly looking at his watch, he exclaimed, brushing aside the photographs with a gesture of regret, " All these are most wonderful, my dear boy, but it is now past five o'clock and I must catch my train home, leaving them to you," and so departed. *Vale Magister Praeclare!*

H. B. B.
W. A. B.

HUGH LONGBOURNE CALLENDAR, 1863–1930.

Hugh Longbourne Callendar, eldest son of the Rev. Hugh Callendar, of Magdalene College, Cambridge, was born at Hatherop, Gloucestershire, on April 18, 1863, and died at Ealing on January 21, 1930. He entered Trinity College, Cambridge, from Marlborough in October, 1882, obtained a First Class in the Classical Tripos at the end of his second year of residence and graduated as a Wrangler in 1885.

Elected a Fellow of Trinity in 1886, he became a Fellow of the Royal Society in 1894 and Rumford Medallist in 1906. He was Professor of Physics at Royal Holloway College from 1888 until 1893, when he was elected Professor at Montreal, in charge of the new Macdonald Physics Building at McGill University. He returned to England in 1898 as Quain Professor at University College, London. In 1902 he succeeded Sir Arthur Rucker at the Royal College of Science, later incorporated in the Imperial College of Science and Technology, where he held the Chair of Physics until his death.

There is good reason to believe that Callendar regarded platinum thermometry and his investigation of the thermal properties of water and steam as his greatest achievements. It therefore seems appropriate that a brief tribute to his memory should confine itself mainly to these aspects of his work.

"It will occupy many specialists in different departments of physics many months to marshal the work of his lifetime into a related whole."

Callendar's development of the platinum resistance thermometer, which made it a standard instrument, is familiar to everyone interested in the precise measurement of temperature. When he began his work at the suggestion of Sir J. J. Thomson, the standard of thermometry was Regnault's normal air thermometer; when it was completed, the claims of the platinum thermometer to be regarded as a superior standard had been established beyond all doubt.

The first serious attempt to construct a platinum resistance thermometer was made by Siemens. Beginning where Siemens had stopped, Callendar planned his work so that the readings of an air thermometer and those of a platinum thermometer could be directly compared. He expressed the results of his experiments in the well-known formula

$$t - pt = \delta\{(t/100)^2 - t/100\},$$

in which the platinum temperature pt is related to the corresponding resistance R by the equation

$$(R - R_0)/(R_{100} - R_0) = pt/100$$

and δ is a constant of which the value depends upon the purity of the platinum employed. He showed that the formula was accurate within 1 per cent. over a range of 600° C.

Hugh L. Callendar

An early consequence of these experiments was his re-determination with E. H. Griffiths of the boiling-point of sulphur. Previously, following Regnault, this temperature had been taken to be 448·34°. As a result of their work, Callendar and Griffiths obtained the value 444·53°, of which they said: "We believe this to be within 0·1° of the true temperature of the vapour of sulphur boiling freely under a pressure of 760 mm."

The records of the General Conference of Weights and Measures, held in Paris in 1927, show how well-founded this conviction was. At this Conference it was agreed to take the temperature of equilibrium between liquid sulphur and its vapour at a pressure of 1 standard atmosphere to be 444·60° C.

At the same Conference it was agreed that, from 0° to 660° C., the temperature t is to be deduced from the resistance R_t of a standard platinum thermometer by the formula

$$R_t = R_0 (1 + At + Bt^2),$$

the constants R_0, A and B being determined by calibration at the air, steam and sulphur points respectively.

This formula corresponds exactly with that established by Callendar in his pioneer paper of 1887.

In an illuminating reference to this remarkable paper, soon after Callendar's death, Sir Richard Glazebrook said: "Nowadays his paper may seem long and unnecessarily detailed, but he had a difficult case to prove, and so the data are given in full, and the reader who has the patience can verify his results himself."

The reader will also find out much about the secrets of Callendar's success. The trouble which he took to acquaint himself with all that had been done before he began and to decide where and how the methods of his predecessors could be improved are as obvious as the printed word can make them. Incidentally, the reader will find here and there, if he looks for them, examples of the whimsical humour and gentle irony which, to those who knew him intimately, were characteristic of the man.

The ingenuity which, in one form and another, was conspicuous in his earliest work was exhibited by Callendar in all that he did.

It is seen again in his compensated resistance thermometer bridge (described in detail in 'Phil. Trans.,' 1902) which, although not constructed in time for his early researches, was subsequently his standard instrument.

In this, everything, including the method of eliminating the effects of temperature change upon the bridge coils, was planned with masterly efficiency. Further, the delicate adjustments necessary to make the instrument satisfy the required conditions were made by himself.

The original bridge, invented in 1887 and constructed in 1893, was used throughout the researches on steam.

A fascinating later example of Callendar's constructive ingenuity was his automatic temperature recorder—a resistance bridge with a "robot" in charge.

In his applications of platinum thermometers, Callendar made great use of the fact that, using two such instruments, the difference between one temperature and another can be determined with ease and certainty from a single reading of a resistance bridge.

He quickly saw the advantages of continuous flow methods in calorimetry, and developed these in practice with consummate skill.

In such methods there are no discontinuities due to the stopping or starting of the flow. The water equivalent of the apparatus is not required. The heat loss can be reduced to a minimum, and its magnitude can usually be obtained, as accurately as desired, by varying the speed and other conditions of flow.

The Joule-Thomson "porous plug," or throttling experiment, is an early example of a continuous flow device to which, incidentally, Callendar applied differential platinum thermometry with conspicuous success.

Callendar applied a similar principle when he invented the continuous flow method of measuring the specific heat of water used by Barnes and himself. At a later date, when the accuracy of the results obtained in these experiments was questioned, he showed his unfailing ingenuity by devising and using what was, in effect, an adaptation of continuous flow to the time-honoured "method of mixtures" familiar to every student of physics.

Another application of the same principle led to the determination of the specific heat of steam. This determination, in conjunction with that of the "cooling effect" in throttling experiments, enabled him to measure the variation with pressure of the total heat of steam.

At a still later date he devised a general method of measuring the total heat at any pressure and temperature. Briefly, this method consisted in throttling to any desired pressure at constant total heat, and then measuring the heat removed (in a continuous flow calorimeter) when reducing the steam to water (at measured temperature) of which the total heat was known.

The same method was used to find the total heat of water, at any temperature and pressure, with reference to that at some temperature and pressure taken as standard. It was also applicable to wet steam.

With high courage Callendar set himself the task of measuring total heats in this way up to and beyond the critical region.

The results are of the greatest interest. Before this work was done it had been commonly supposed that, at the critical point, the differences between saturated steam and water disappear. The specific volumes, it was thought, were then identical, and the latent heat of vaporisation zero.

As is well known, the simplest method of determining the critical temperature of a liquid is to heat an appropriate amount of it in a sealed glass tube, and to note the temperature at which the meniscus, separating liquid from vapour, disappears. This method presents no difficulties with substances like CO_2 and SO_2; but until fused-quartz tubes became available, it was impracticable to apply it to water owing to the disintegrating effect of the latter upon ordinary glass.

In agreement with other observers, Callendar found the critical temperature of water, using quartz-glass tubes, to be 374° C. Using different quantities of water in separate tubes of similar volume, he also obtained values for the densities of the liquid and the saturated vapour at temperatures below the critical point by observing the temperatures at which the tubes became filled with the liquid or the vapour, as the case might be.

Similar experiments can be performed very easily, using liquid SO_2 instead of water. In this case ordinary glass suffices, and the critical temperature and pressure are so much lower than those of water that there is neither difficulty nor danger in observing what happens in a series of tubes like those used by Callendar. Anyone who has performed such experiments and compared the phenomena with those exhibited by liquids, which do not mix at ordinary temperatures, but become miscible when heated in all proportions at higher temperatures, will agree with the view that the temperature at which the meniscus vanishes, in the case of a single substance in the tube, is not necessarily that at which the liquid and vapour phases become identical. It was left to Callendar to produce quantitative evidence of the required kind.

He found, for example, that the latent heat of vaporisation of water at the critical temperature is not zero but 72·4 cal./gm. Not until a temperature of 380·5° C. is reached, does the latent heat vanish. In this work, based upon measurements of total heat, special methods had to be devised in the case of water to prevent contamination by air, of which very small quantities were enough to make accurate measurements impossible.

Any attempt to indicate the character of Callendar's work on steam must contain some reference to the analytical skill which he displayed on the theoretical side.

Almost every equation he used to correlate his results had a reasoned, if not entirely rigorous, basis. His equations, unlike those of his predecessors, were all consistent with the laws of thermodynamics.

One of the earliest applications which he made of platinum thermometry was to the study, at Montreal, in conjunction with Nicolson, of the law of pressure-temperature variation in the adiabatic expansion and contraction of dry steam.

This led him to the formulation of his well-known characteristic equation for an imperfect gas, which, in its earliest form :—

$$v - b = \mathrm{R}\theta/p - a/\mathrm{R}\theta^n$$

was a modification of the Rankine-Thomson equation. Following previous workers, he replaced their v by $(v - b)$. The novelty lay in the substitution of θ^n for θ^2 in the last term.

Assuming, as the simplest hypothesis suggested by the kinetic theory, that the variable part of the internal energy u of a gas is proportional to $p\,(v - b)$, and applying the second law of thermodynamics, the Callendar equation leads to the expression

$$u = np\,(v - b) + \text{const.}$$

and to expressions for n, in terms of definable quantities of which the simplest are :—

$$n = (c_v)_0/\mathrm{R} \text{ and } (n + 1) = (c_p)_0/\mathrm{R},$$

$(c_v)_0$ and $(c_p)_0$ being the values to which the specific heats at constant volume and constant pressure, respectively, approach when the pressure is reduced without limit.

It also followed that the pressure-temperature variations for adiabatic changes should be given by the equation

$$p/\theta^{n+1} = \text{const.}$$

This was in accord with the experimental results for dry steam, and the experimental value for n did not differ greatly from that calculable from the kinetic theory by an approximate method.

Correspondingly simple expressions for the total heat H and the entropy ϕ were :—

$$\mathrm{H} = (n + 1)\,p\,(v - b) + bp + \text{const.} \qquad (1)$$

and

$$\phi = (n + 1)\,\mathrm{R} \log \theta - \mathrm{R} \log p - ncp/\theta + \text{const.}$$

in which c represents the value of $a/\mathrm{R}\theta^n$.

It was characteristic of the man that he should try to find a simple physical interpretation of c.

Writing his equation in the form

$$v - b = \mathrm{R}\theta/p - c,$$

he pointed out that $\mathrm{R}\theta/p$ represents the volume which the vapour would occupy if the "effective" volume were correctly represented by $(v - b)$ and if the vapour behaved like an ideal gas, consisting of molecules of the simplest possible type, R being the appropriate "gas constant." The presence of the term c shows that the actual volume is less than the ideal volume. He suggested that the discrepancy is due to the fact that the vapour does not consist wholly of simple molecules, but contains also a certain proportion of molecular aggregates. Increase in the number of such "molecules" of greater mass would cause $\mathrm{R}\theta/p$ to become increasingly greater than the ideal volume. In this interpretation, inter-molecular forces do not appear explicitly. They are replaced by molecular complexes, of which, however, they may be the cause.

Another striking example of Callendar's ingenuity is his equation for the total heat of water, which he used with great success in his correlation of the facts. To obtain it he developed a particular form of an argument previously used by Poynting, and assumed that water in equilibrium with its saturated vapour contains the same number of vapour molecules per unit volume as the vapour itself. He then supposed that the formation of such vapour molecules, within the liquid, consumed the same amount of heat as would be required to produce the corresponding volume of steam. Hence his equation

$$h = st + w\mathrm{L}/(v - w) \qquad (2)$$

expressing the value of the total heat of water at t °C., reckoned from that at the freezing point as zero. In this, w and v are the specific volume of water and the saturated vapour respectively, and L is the latent heat of vaporisation, at the temperature t. The constant s was fixed by taking h to be 100 calories at 100° C.

The equation leads to an expression for the entropy of saturated steam which, with the expressions for H and ϕ, already mentioned, gives an equation connecting the saturation pressure of steam with the temperature. This well-known equation contains nothing, in addition to b and c, that is not directly measurable, and is in close accord with experiment up to 200° C. Beyond this, the experimental results began to deviate appreciably from those calculated, and it became necessary to regard c as a function involving the pressure as well as the temperature.

In order to maintain thermodynamic consistency between the equation of state and the expression for the internal energy, it is necessary that the relation between c, p and θ should satisfy certain conditions. From the many possible forms which the relation might take, Callendar selected the simplest for his purpose. It is contained in the equation

$$v - b = \mathrm{R}\theta/p - c/(1 - \mathrm{Z}^2) \qquad (3)$$

in which $c = a/\mathrm{R}\theta^n$ as before, and $\mathrm{Z} = kcp/\theta$, where k is an additional constant.

He found that the experimental curve for the density of the saturated vapour could be represented by this equation right up to the critical temperature, without alteration of the value of c, provided that the value of the constant k were chosen to fit the density at that temperature. Further, the temperature-pressure curve for saturated vapour, the easiest of all the curves to determine experimentally, gave values which were in close agreement, not only with those which could be deduced from his theoretical equation, but also with those obtained by other observers, by other methods, up to 374° C. The theoretical equation continued to give values of p agreeing with those observed by himself, until the temperature at which saturated steam and water become indistinguishable was attained.

Finally, the equation

$$(H - st)/(h - st) = v/w,$$

in which $H = h + L$, following at once from equation (2), gave a relation connecting total heats and specific volumes, which was used with success to test the accuracy of the measurements made in the critical region.

Callendar's last words on the practical aspects of this great work, which he pursued untiringly, will be found in his Hawksley Lecture, delivered to the Institution of Mechanical Engineers shortly before his death. Referring to his three fundamental equations (1, 2 and 3 above), he said: "They constitute the only rational and consistent standard which has yet been proposed for steam, and would suffice for all practical requirements if they were generally adopted."

Beyond doubt it was conviction and not dogmatism which impelled him to use these words, just as it was resignation and not impatience which led him to add: "But it has taken thirty years to reach international agreement with regard to the temperature scale, which is a much less exacting problem, and we may have to wait a long time before other nations are prepared to accept such a simple and unpretentious scheme."

Not the least of Callendar's many accomplishments was the dexterity with which he could place his views before an audience. His capacity in this direction impressed every student who attended his lectures, models of clearness and precision as they were; but his public addresses were as infrequent as he could make them.

The skill he could command and use in this direction was seen to great advantage in a remarkable address which he delivered to the Physical Society, as its President, in 1911. In this address, with an engaging display of enthusiasm for the task, he endeavoured to show how, but for the errors in the experimental data of others upon which he had to rely, Carnot's exposition of the relation between motive power and heat would have been the precise equivalent of what has come to be established doctrine.

Perhaps the most striking feature of this address was the plea for the retention of the concept of "caloric" which it contained.

Referring to the Carnot equation connecting the motive power with the amount of caloric involved and with the temperatures of entry and escape, Callendar maintained that it leads to the simplest possible picture of the way in which a heat engine operates. It shows at once that the production of work from heat is due not to an actual consumption of caloric, but to the transport of caloric from a higher to a lower temperature. Caloric is not itself motive power, but is capable of performing work under suitable conditions in virtue of its tendency to flow down a temperature gradient.

The simplicity of this picture was lost, according to the address, when at a later date the calorimetric or energy measurement of heat was introduced, and entropy took the place of caloric in the Carnot cycle equation. "No one at that time (1865) appears to have appreciated Carnot's solution, or to have realised that entropy was merely caloric under another name."

It has been suggested that Callendar could scarcely expect to be taken seriously in all that he advocated in this address. Whether this be true or not, the young student of thermodynamics cannot fail to find both pleasure and profit in a perusal of its contents; particularly if he can succeed, even temporarily, in banishing kinetic theory pictures from his mind.

For example, he cannot fail to be impressed by the directness, compared with others, of the proof by Carnot's method that all reversible engines working between the same temperature limits have the same efficiency. "We have become so saturated with the idea that heat is energy, and must be measured in units of energy, that we are apt to forget that a quantity of heat is not completely specified by its energy equivalent."

To those who knew Callendar only in his maturer years, Mr. Upcott's account (*The Times*, January, 1930) of his school days at Marlborough is a captivating narrative. We are told he had that versatility of talent that does all things easily, that he was the first mathematician in the school, in the first rank in classics, and that, of his own accord, he spent hours in the school laboratory, and read all the scientific books in the library. Already his inventive genius had shown itself in diverse directions. Yet he was no recluse, but took his part in all school activities, and was universally popular. He played for his house at football, and was in the Rifle Corps eight and in the gymnasium eight for three years. "He had gentle and winning manners, a most attractive face, and modesty."

At Cambridge Callendar continued to excel at sport, being in the University lawn tennis team and captain of the lacrosse team. He also captained the shooting eight, and represented the University at gymnastics.

Though it was difficult to persuade him to play towards the end, he retained his skill and interest in lawn tennis throughout his life. In his later years he was fond of watching the play at tournaments, in which members of his family were taking part, Mrs. Callendar and each of his three sons being, like himself, an enthusiastic exponent of the game. He took a passive interest in golf, but regarded the time the game demanded as a fatal objection to its active pursuit.

It was natural that he should be interested in motoring from the first. He began by taking up motor-cycling as a hobby soon after his return from Canada, and made many contributions towards the improvement and testing of motor design. An early car of his—with contrivances added by himself to increase its efficiency and to make it more weatherproof—invited attention by its unconventional appearance. Its owner drove it with complete equanimity.

In an appreciation of his work for engineering, Professor Dalby has said: "Though we all recognised Callendar as a genius moving in altitudes of thought denied to most of us, yet he was such a lovable character, so simple-minded and so ready to help, that we forgot the genius, and remembered only the man and the friend."

Callendar's friendliness and entire freedom from affectation of any kind, with no hint of superiority in anything he said or did, made a deep impression upon everyone who knew him.

S. W. J. S.

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END OF THE ONE HUNDRED AND THIRTY-FOURTH VOLUME (SERIES A).

I. A. R. I. 75

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